OAR Box 1827

Prepped by Charmelle Mathews

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Environment   Environnement
Canada   Canada

Conservation and   Conservation et
Protection   Protection

Ottawa, Ontario
K1A 0H3

July 17, 1990

JUL 2 0 1990

Air Docket (LE-131)
Environmental Protection Agency
Room M-1500
401 M Street S.W.
Washington, D.C.
U.S.A.   20460

RECEIVED
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EPA AIR DOCKET

Sir/Madam:

I would like to thank EPA for affording us the
opportunity to comment on the Fuels and Fuel Additives
Waiver Application by Ethyl Corporation for use of MMT in
unleaded gasoline in the United States. Our comments are
a provision of information on the Canadian experience with
MMT rather than direct comments on Ethyl's application.

Ethyl Corporation mentioned a number of times in
its application, the extensive use of MMT in unleaded
gasoline in Canada. There are differences between Canada
and the U.S. that must be considered when evaluating the
Canadian experience. There are no inspection and
maintenance (I&M) programs in Canada as you have in the
U.S. Also, when compliance testing for emissions on new
automobiles is conducted, MMT-free fuel is used to ensure
consistency with the U.S. Standard (adopted by Canada).
There is no compliance testing for on-road vehicles.

We have had concerns about MMT plugging
catalysts. However, while it is certain that some
catalysts plug with MMT, we have concluded the number is
relatively small. Transport Canada has made repeated
requests for data on the incidence of catalyst plugging
but no manufacturer has yet submitted any data. Also,
examination of the manufacturer's warranty claims did not
reveal any abnormal incidence of plugging.

Because Canada has no I&M programs, catalyst
plugging for vehicles off warranty is difficult to
enumerate. Also, some provinces do not have legislation
prohibiting tampering and those that do, have limited
enforcement. Therefore, a plugged catalyst would simply
be removed and no complaint made to manufacturers.

Canada

- 2 -

Health and Welfare Canada has evaluated the possible health effects of using MMT in gasoline. That department has advised Environment Canada there would be no significant increase of manganese in the environment to affect human health by the use of MMT in gasoline. Ms. Grace Wood (613) 957-1503 can be contacted for more details.

We have already passed some printed material to Ms. Marilyn McCall of Mobile Sources. Additional material on ambient data is enclosed and the list of names and telephone numbers of the contacts is attached.

Finally, based on data reported by refiners to Environment Canada, MMT is used at the maximum of 18 milligrams per litre of unleaded gasoline allowed by the Canadian General Standards Board specifications. In Canada, refiners are octane stressed because most are phasing out leaded fuel production to comply with new regulations to take effect on December 1, 1990.

I hope the information provided is helpful and can be used for evaluating Ethyl's application.

Yours sincerely,

J.A. Buccini
Director
Commercial Chemicals Branch

c.c.:   Laura Tupper, IPB
        Lui Hrabelski, Transport Canada
        Grace Wood, Health & Welfare Canada

Report	Contact
Inhalable Particulate Matter (PM_{10}) Sampling Network (1984–1987) Trends in Ambient Manganese Levels (MMT)	Tom Dann (613) 991-0459
Air Quality in Ontario 1988	Phil Kiely (416) 235-5780
National Inventory of Sources and Emissions of Manganese – 1984	Art Jaques (819) 994-3098

A. 90-16
IV-D-181

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Conservation and   Conservation et
Protection   Protection

Ottawa, Ontario
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| Government of Canada | Gouvernement du Canada | MEMORANDUM | NOTE DE SERVICE |

TO / A

┌ ┐
V. Shantora
Chief
Transportation Systems Division
13th Floor, PVM
└ ┘

FROM / DE

┌ ┐
A/Chief
Pollution Measurement Division
Room 105A, RRETC
└ ┘

SECURITY - CLASSIFICATION - DE SÉCURITÉ	
OUR FILE/NOTRE RÉFÉRENCE	
4024-23	
YOUR FILE/VOTRE RÉFÉRENCE	
DATE	**August 15, 1984**

SUBJECT / OBJET

Trends in Ambient Manganese Levels (MMT)

Please find attached some data from selected Ontario monitoring sites showing trends in ambient manganese concentrations. It is apparent that there has been a strong downward trend since 1969 at all sites. Sites in the vicinity of strong point sources ie. Hamilton, Welland exhibit higher concentrations than those in the vicinity of roadways ie. Toronto, (Evans and Arnold).

I have talked to A. Sheffield about inventory data for manganese and I believe information on transportation related emissions of manganese will be forthcoming. If any further data analysis is required please let me know.
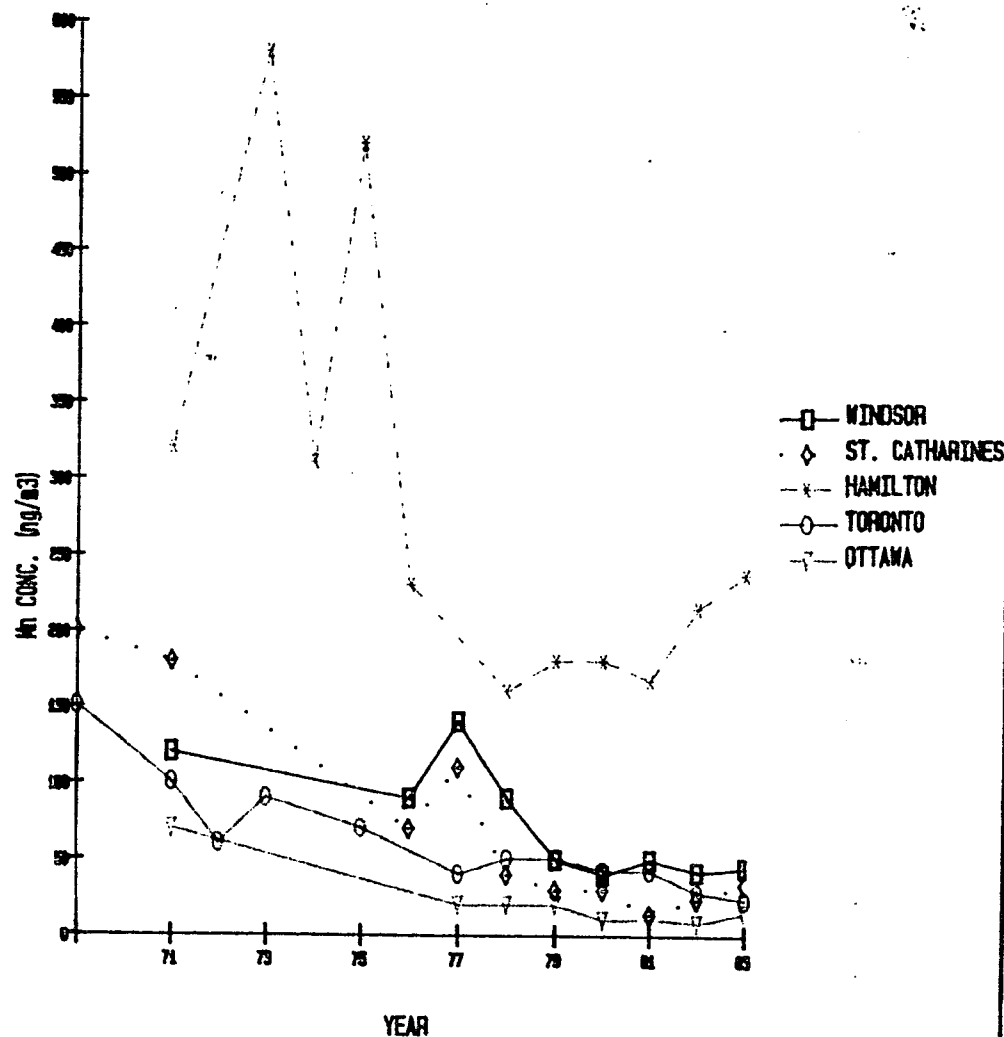
T. Dann

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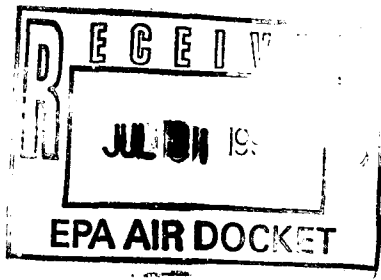
TD/vs

Att

cc: A. Sheffield
     D.A. Williams

AMBIENT MANGANESE TRENDS
ONTARIO STATIONS

Mn CONC. (ng/m3) vs YEAR

Legend:
- —□— WINDSOR
- · ◇ · ST. CATHARINES
- —×— HAMILTON
- —○— TORONTO
- —▽— OTTAWA

HISTORICAL MANGANESE LEVELS
(ng/m3)

0 YEAR	1 WINDSOR 467 UNIV. AVE.	2 ST. CATHARINES 71 KING	3 HAMILTON BART./KENT.	4 TORONTO EVANS/ARNOLD	5 OTTAWA MCD. GDNS.
1 1969		200		150	
2 1970					
3 1971	120	180	320	100	70
4 1972				60	
5 1973			560	90	
6 1974			310		
7 1975			520	70	
8 1976	90	70	230		
9 1977	140	110		40	20
10 1978	90	40	160	50	20
11 1979	50	30	180	50	20
12 1980	40	30	160	42	10
13 1981	50	14	167	42	11
14 1982	42	24	215	28	8
15 1983	45	34	237	23	15

85-87   33   23

Montreal Duncan/Deane — 33
(85-87)

Table A15 : Mean Concentration (µg/m³) of Manganese (Mn)   1985 - 1987

Station Number	City	No. of Samples	Coarse	Fine	Total	F/C Ratio	Std. Dev. of Ratio
30101	HALIFAX	50	0.007	0.010	0.016	1.73	0.94
50104	MONTREAL	56	0.020	0.033	0.053	2.01	0.90
50109	MONTREAL	40	0.036	0.047	0.083	1.49	0.53
50307	QUEBEC CITY	53	0.010	0.014	0.024	1.74	0.84
60104	OTTAWA	47	0.010	0.013	0.023	1.58	0.78
60417	TORONTO	41	0.013	0.015	0.028	1.40	0.49
70119	WINNIPEG	40	0.009	0.008	0.017	1.19	1.10
90130	EDMONTON	34	0.019	0.012	0.031	0.77	0.48
90204	CALGARY	49	0.012	0.013	0.025	1.08	0.49
00118	VANCOUVER	38	0.010	0.024	0.035	2.49	0.93
00111	VANCOUVER	68	0.013	0.018	0.031	1.59	1.01
00303	VICTORIA	54	0.006	0.013	0.020	2.21	1.24
60204	WINDSOR	67	0.017	0.015	0.033	1.03	0.60
61901	WALPOLE ISLAND	23	0.006	0.004	0.010	0.73	0.62

HISTORICAL MANGANESE LEVELS
### (ng/m3)

YEAR	WINDSOR 467 UNIV. AVE.	SARNIA GEN. HOSP.	LONDON KING/RECT.	ST. CATHARINES 71 KING	WELLAND PS 309	HAMILTON NORTH PARK	HAMILTON BART./WENT.	TORONTO 67 COLLEGE
1969		70		200				40
1970								
1971	120	50	70	180		320	320	70
1972					13410			
1973					7710	360	580	
1974					6950		310	
1975					540	170	520	
1976	90			70	800	380	230	30
1977	140	30	30	110				
1978	90	40	40	40		260	160	30
1979	50	40	50	30		230	180	30
1980	40	30	20	30		290	180	20
1981	50	26	19	14		169	167	13
1982	42	22	19	24		147	215	24
1983	45	28	24	34		150	237	20

```
                                   (ng/m3)

YEAR        TORONTO          OTTAWA
            EVANS/ARNOLD     MCD. GDNS.
---------------------------------------------------------------
------
1969          150
1970
1971          100              70
1972           60
1973           90
1974
1975           70
1976
1977           40              20
1978           50              20
1979           50              20
1980           42              10
1981           42              11
1982           28               8
1983           23              15
```

APPENDIX

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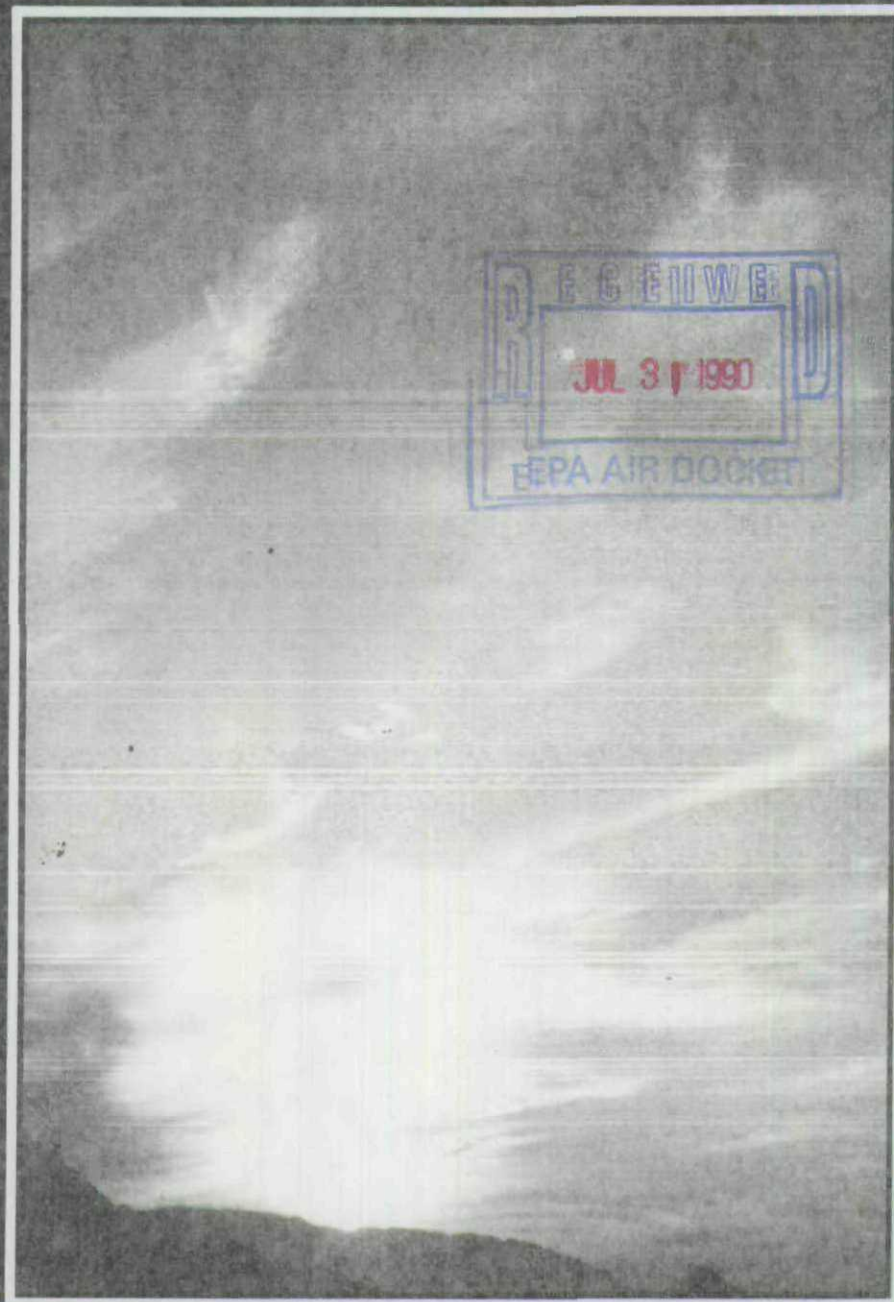
Air Quality in Ontario
1988

Environment
Environnement

Ontario   Jim Bradley, Minister/ministre

TABLE A-31 MANGANESE (Mn) STATISTICS (1988)

ONTARIO MINISTRY OF THE ENVIRONMENT - AIR RESOURCES BRANCH

YEAR - 1988   POLLUTANT - MANGANESE IN TOTAL SUSPENDED PARTICULATE   UNIT - .001 MICROGRAMS/CU.METRE

STATION NUMBER	LOCATION	NO OF SAMPLES	PERCENTILES 10	30	50	70	90	99	MAX	ARITH MEAN	GEOM MEAN	TIMES ABOVE CRITERIA 24-HR
12002	CITY HALL, 444 WINDSOR AV WINDSOR	53	30	40	50	80	136	217	250	68	55	0
12005	7730 RIVERSIDE DR E WINDSOR	52	20	20	30	60	90	120	120	43	33	0
12008	467 UNIVERSITY AV W WINDSOR	340	20	40	60	80	140	248	350	72	57	0
12010	SEWAGE STN, HANNING RD WINDSOR	49	10	10	20	30	80	138	170	32	22	0
12011	DROUILLARD RD/RICHMOND ST WINDSOR	29	30	54	90	112	162	292	310	97	78	0
12013	FILTRAT PLT,3665 WYANDOTTE ST E WINDSOR	54	40	60	110	312	861	1302	1350	289	141	0
12015	SEWAGE STN, HWY 18/PROSPECT WINDSOR	50	50	60	95	140	180	220	220	106	92	0
12038	2885 HOWARD AV WINDSOR	57	40	68	90	150	214	279	290	113	94	0
12039	DOUGLAS ST/E.C. ROW W WINDSOR	59	40	50	60	80	120	140	140	69	64	0
12047	DORWIN PLAZA, DOUGALL AV WINDSOR	56	30	40	50	70	110	144	150	60	52	0
12049	643 ALEXANDRINE WINDSOR	61	20	30	40	60	100	141	160	54	45	0
12051	604 CAPITOL/REMINGTON WINDSOR	56	20	30	50	80	120	143	160	62	50	0
13003	POST OFFICE, 10 CENTRE ST CHATHAM	58	10	20	20	20	50	74	80	25	22	0
14016	HWY40 (OPP LAMBTON GS) COURTRIGHT	350	5	10	10	20	30	50	70	17	13	0
14030	RR1 (W OF HOUSE) CORUNNA	56	5	5	12	20	40	54	60	17	12	0
14031	RR1 (W OF BARN) MOORETOWN	55	5	5	10	20	30	44	50	14	11	0
14064	CENTENNIAL PK,FRONT ST/CN TRACKS SARNIA	58	5	20	30	40	83	124	130	35	24	0
14152	CHRISTINA/EXMOUTH ST SARNIA	115	20	40	60	98	486	1473	2180	167	77	0
14153	704 MARA ST POINT EDWARD SARNIA	115	10	20	30	58	197	835	1170	90	38	0
15001	WRN FAIR GROUNDS, KING/RECTORY LONDON	60	10	20	30	40	60	111	130	35	28	0
15009	LONGWOODS CONSERVATION AUTHORITY	65	5	5	10	20	36	60	60	17	13	0
15014	POND MILLS RD/DEVERON CRES LONDON	57	10	20	30	40	70	90	90	36	30	0
15015	951 COMMISSIONERS RD E LONDON	58	10	20	20	30	50	64	70	27	23	0
15016	801 COMMISSIONERS RD E LONDON	59	10	20	20	30	40	64	70	23	19	0
15017	8 MOUNTSFIELD DR LONDON	56	10	20	30	30	60	88	100	30	24	0
15116	801 COMMISSIONERS RD E LONDON	40	14	21	28	36	50	78	80	32	27	0

TABLE A-31 (Cont.)

ONTARIO MINISTRY OF THE ENVIRONMENT - AIR RESOURCES BRANCH

RUN DATE
JUL 25, 1989

YEAR - 1988   POLLUTANT - MANGANESE IN TOTAL SUSPENDED PARTICULATE   UNIT - .001 MICROGRAMS/CU.METRE

STATION NUMBER	LOCATION	NO OF SAMPLES	PERCENTILES 10	30	50	70	90	99	MAX	ARITH MEAN	GEOM MEAN	TIMES ABOVE CRITERIA 24-HR
22907	RAINHAM RD (NEAR STELCO GATE) NANTICOKE	57	46	70	140	182	398	1184	1450	199	126	0
26029	EDNA/FREDERICK STS KITCHENER	60	20	40	50	60	91	179	230	55	46	0
27008	71 KING ST ST CATHARINES	59	5	20	40	50	70	108	120	39	30	0
29011	BURLINGTON/LEEDS HAMILTON	52	180	303	430	540	765	1234	1260	452	377	0
29012	BURLINGTON/WELLINGTON HAMILTON	56	50	75	100	150	235	528	550	134	101	0
29017	CHATHAM/FRID HAMILTON	54	53	90	135	171	297	408	430	151	123	0
29025	BARTON/WENTWORTH HAMILTON	43	70	100	150	310	648	2224	3830	337	188	0
29067	450 HUGHSON ST N HAMILTON	54	20	40	65	100	207	403	430	95	63	0
29098	BAY/MAIN ST HAMILTON	51	20	40	50	90	270	508	550	108	64	0
29102	467 BEACH BLVD HAMILTON	63	122	230	330	394	620	807	890	336	269	0
29114	VICKERS RD/EAST 18TH ST HAMILTON	46	10	30	45	60	112	245	250	56	40	0
31104	26 BREADALBANE TORONTO	340	20	30	40	50	80	106	150	46	40	0
31120	PERTH/RUSKIN(JUNCTION TRIANGLE) TORONTO	111	20	30	40	50	70	107	110	39	34	0
44005	2487 LAKESHORE E/BIRKBANK RDS OAKVILLE	124	11	16	28	40	71	119	130	34	25	0
45080	FINLEY RD, ANIMAL HOSPITAL AJAX	93	20	36	50	60	90	121	130	55	47	0
45081	65 HARWOOD AVE, AJAX WORKS DEPT AJAX	83	20	20	40	50	68	100	100	40	34	0
63005	HOSP, ARCHIBALD/ARTHUR STS THUNDER BAY	55	5	10	30	40	66	94	100	31	21	0
63022	HOSPITAL, 35 ALGOMA ST N THUNDER BAY	56	5	20	30	40	50	84	90	31	25	0
71042	PUMPHOUSE, BONNEY ST SAULT STE MARIE	267	100	208	330	642	1270	1923	2650	526	348	0
71049	LAND OFFICE, QUEEN ST SAULT STE MARIE	59	20	40	50	86	190	240	240	76	58	0
71068	WM. MERRIFIELD SCHOOL SAULT STE MARIE	114	20	39	70	130	291	540	830	118	68	0
71071	BOUNDRY RD/BENNET SAULT STE MARIE	29	9	10	20	30	60	80	80	27	20	0
71072	FIRST AV/SECOND LINE SAULT STE MARIE	109	20	30	50	86	142	370	400	74	52	0
72077	MINISTRY OF HEALTH BLDG TIMMINS	40	10	16	20	30	51	96	100	26	20	0
75010	OPP STN NORTH BAY	36	5	10	20	20	20	60	60	18	15	0
77016	WATER TANK, ASH ST SUDBURY	56	5	7	10	20	30	40	40	15	12	0

TABLE A-31 (Cont.)

STATION NUMBER	LOCATION										
	NORTH BAY	36	5	10	20	20	20	60	60	18	15	0
77016	WATER TANK, ASH ST										
	SUDBURY	56	5	7	10	20	30	40	40	15	12	0

TABLE A-31 (Cont.)

ONTARIO MINISTRY OF THE ENVIRONMENT - AIR RESOURCES BRANCH

YEAR - 1988   POLLUTANT - MANGANESE IN TOTAL SUSPENDED PARTICULATE   UNIT - .001 MICROGRAMS/CU.METRE   RUN DATE

STATION NUMBER	LOCATION	NO OF SAMPLES	PERCENTILES						MAX	ARITH MEAN	GEOM MEAN	TIMES ABOVE CRITERIA 24-HR
			10	30	50	70	90	99				
77026	19 LISGAR ST											
	SUDBURY	54	5	10	20	30	40	54	60	21	17	0

MAP 1   LOCATIONS OF CONTINUOUS MONITORING - S. ONTARIO

- OTTAWA
- CORNWALL
- DORSET
- BARRIE
- PETERBOROUGH
- KINGSTON
- TIVERTON
- ALLISTON
- STOUFFVILLE
- OSHAWA
- GUELPH
- TORONTO
- MISSISSAUGA
- WATERLOO
- OAKVILLE
- KITCHENER
- BURLINGTON
- HURON PARK
- HAMILTON
- ST CATHARINES
- THOROLD
- PARKHILL
- CHIPPAWA
- SARNIA
- NIAGARA FALLS
- MANDAUMIN
- LONDON
- COURTRIGHT
- LONGWOODS
- SIMCOE
- NANTICOKE
- LONG POINT
- WINDSOR
- MERLIN

CONTINUOUS SITES
S. ONTARIO - 1988

MAP 2   LOCATIONS OF CONTINUOUS MONITORING - N. ONTARIO

National Inventory of Sources and Emissions of Manganese - 1984

Report EPS 5/MM/1
May 1987
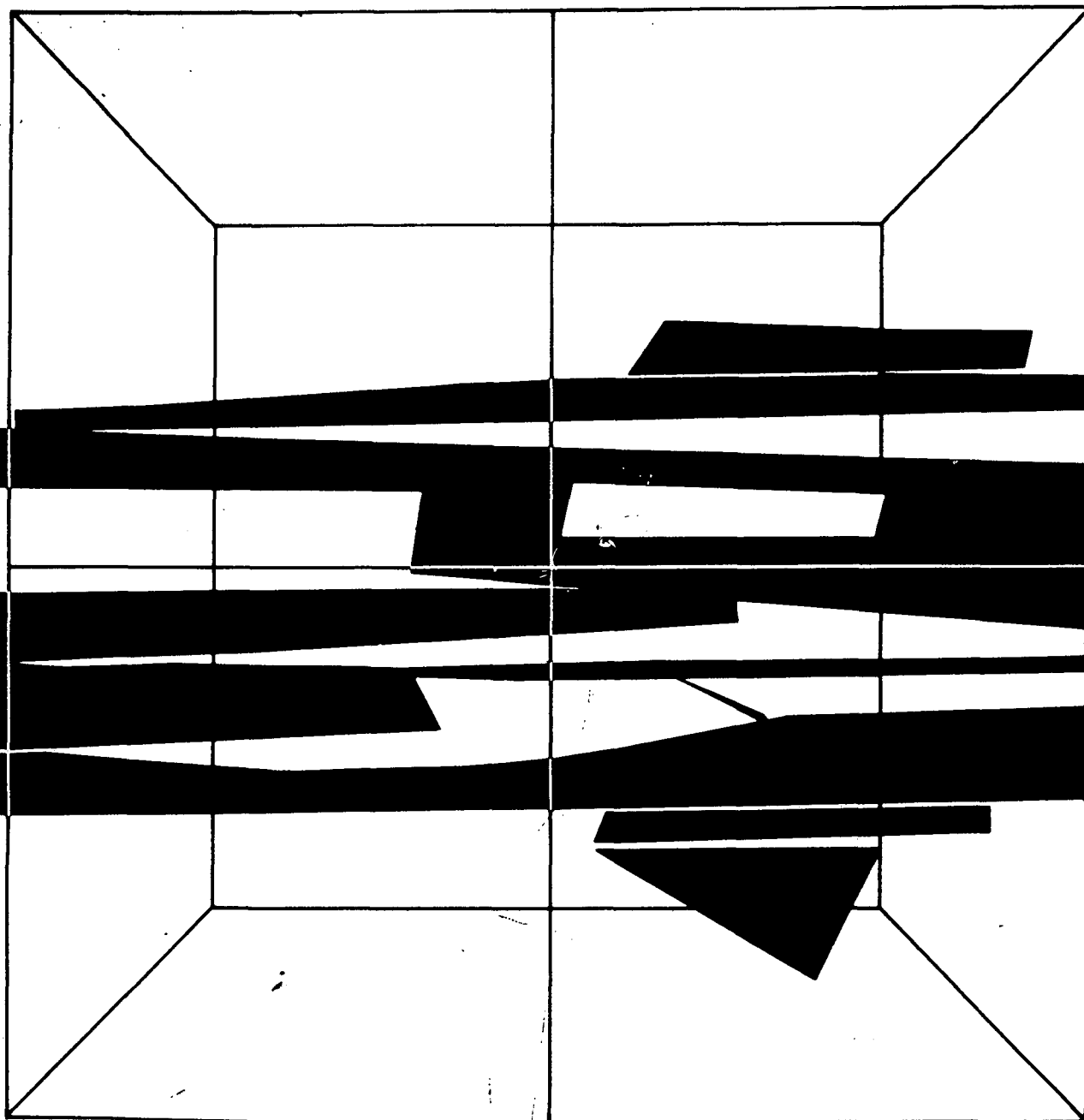
Environment   Environnement
Canada   Canada

Canada

ENVIRONMENTAL PROTECTION SERIES REPORTS

Sample Number:

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[EPS]  [3] / [HA] / [1]
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————Number of report having qualifiers EPS 3/HA

————Subject Area Code

————Report Category

————Environmental Protection Series
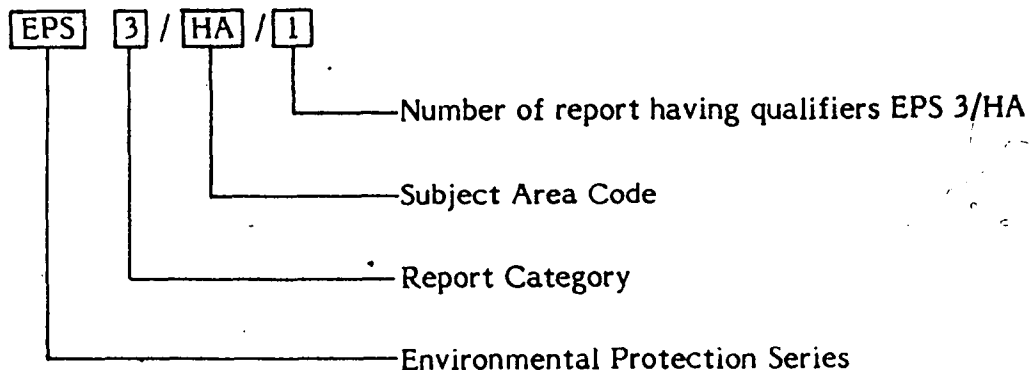
Categories		Subject Areas	
1	Regulations/Guidelines/Codes of Practice	AG	Agriculture
2	Public Consultation: Problem Assessment, Control Options	AP	Airborne Pollutants
		AT	Aquatic Toxicity
		CC	Commercial Chemicals
3	Research and Technology Development	CE	Consumers and the Environment
		CI	Chemical Industries
4	Literature Reviews	FA	Federal Activities
5	Surveys	FP	Food Processing
6	Social, Economic and Environmental Impact Assessments	HA	Hazardous Wastes
		IC	Inorganic Chemicals
		MA	Marine Pollution
7	Surveillance	MM	Mining & Ore Processing
8	Policy Proposals & Statements	NR	Northern & Rural Regions
9	Manuals	PF	Paper and Fibres
		PG	Power Generation
		PN	Petroleum and Natural Gas
		SF	Surface Finishing
		SP	Oil & Chemical Spills
		SRM	Standard Reference Methods
		TS	Transportation Systems
		UP	Urban Pollution

New subject areas and codes are introduced as they become necessary. A list of EPS reports may be obtained from Environmental Protection Publications, Conservation and Protection, Environment Canada, Ottawa, Ontario, Canada, K1A 0E7.

Printed in Canada

NATIONAL INVENTORY OF SOURCES AND EMISSIONS OF MANGANESE (1984)

by

A.P. Jaques
Environmental Analysis Branch
Environmental Protection
Conservation and Protection
Environment Canada

READERS' COMMENTS

Readers who wish to comment on the contents of this report may address their comments to:

Mr. A.P. Jaques
Environmental Analysis Branch
Environmental Protection
Conservation and Protection
Environment Canada
Ottawa, Ontario
K1A 0E7

iii

ABSTRACT

Estimates of the quantities of manganese released to the environment as emissions in 1984 are summarized in this report. Emissions have been classified by source, sector and province. The data presented are estimates based on source testing data, process emission factors and production figures. Total anthropogenic emissions of manganese in 1984 were estimated at 1225 tonnes, with manganese-bearing alloy production accounting for 47% of the total.

A brief summary of the sources and uses of manganese has been included as well as a summary of the health effects of manganese. The methods used to estimate emissions and the accuracy of the data recorded have been described.

v

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

This inventory identifies anthropogenic sources of manganese released to the environment as emissions. For the purposes of this report emissions, have been defined as gaseous or particulate releases to the atmosphere.

Manganese emissions in Canada for 1984 have been estimated and expressed as elemental manganese (Table S.1). Figures S.1 and S.2 provide a breakdown of emissions by province and source.

Total anthropogenic emissions of manganese in 1984 were estimated to be 1225 tonnes. Production of ferromanganese and silicomanganese accounted for an estimated 576 tonnes or 47% of the total. Emissions from the production of iron and steel were estimated to be 337 tonnes (28%); gasoline-powered motor vehicles 211 tonnes (17%); and iron and steel foundries 40 tonnes (3%) of the total emissions for 1984. The remaining 5% of emissions were contributed by other miscellaneous sources.

Comparison of the data in this report with data for previous years indicates that emissions from gasoline combustion have remained relatively constant throughout the 1980s. Emissions from the ferroalloy industry, have declined considerably from the early 1970s due to the addition of more efficient emission controls.

TABLE S.1   SUMMARY OF MANGANESE EMISSIONS IN 1984 (tonnes)

Sector	Nfld.	P.E.I.	N.S.	N.B.	Que.	Ont.	Man.	Sask.	Alta.	B.C.	Terr.	Canada	% of Total
Industrial Processes:													
Manganese - bearing Alloy Production					576							576	47.0
Primary Copper and Nickel Production					< 1	<1	< 1			< 1		< 1	< 0.1
Primary Zinc Production					< 1	<1	< 1			< 1		< 1	< 0.1
Primary Iron and Steel Production			6		57	229	6	21	16	2		337	27.5
Iron and Steel Foundaries		<1	1	<1	6	29	2	< 1	1	1		40	3.3
Battery Manufacturing						< 1	< 1					1	0.1
Cement Manufacturing	<1		< 1	< 1	4	1	< 1	< 1	1	< 1		7	0.6
Metallurgical Coke Manufacturing			< 1			< 1		< 1		< 1		< 1	< 0.1
Non-ferrous Alloys					< 1	< 1						< 1	< 0.1
Welding Rods					< 1	< 1						< 1	< 0.1
Miscellaneous Sources	-	-	-	-	-	-	-	-	-	-	-	N/A	-
Fuel Combustion - Stationary Sources:													
Power Generation	<1	<1	<1	<1	< 1	4	<1	4	5	< 1	<1	14	1.2
Industrial Fuel Combustion	<1	<1	<1	<1	< 1	1	1	< 1	< 1	< 1	<1	3	0.2
Commercial Fuel Combustion	<1	<1	<1	<1	< 1	< 1	<1	< 1	< 1	< 1	<1	< 1	< 0.1
Residential Fuel Combustion	<1	<1	2	<1	< 1	< 1	<1	< 1	1	< 1	<1	3	0.2
Fuel Combustion - Transportation Sources:													
Gasoline-powered Motor Vehicles	4	1	7	7	42	71	10	12	29	27	1	211	17.2
Solid Waste Incineration:													
Municipal Refuse Incineration		<1			3	2				< 1		5	0.4
Sewage Sludge Incineration						< 1				< 1		< 1	< 0.1
Miscellaneous Sources:													
Pesticide Application[a]												28	2.3
Totals[b]	4	1	17	7	688	338	20	37	53	31	1	1225	100

[a]   Distribution as follows: Maritimes 12; Ontario/Quebec 12; West 4.
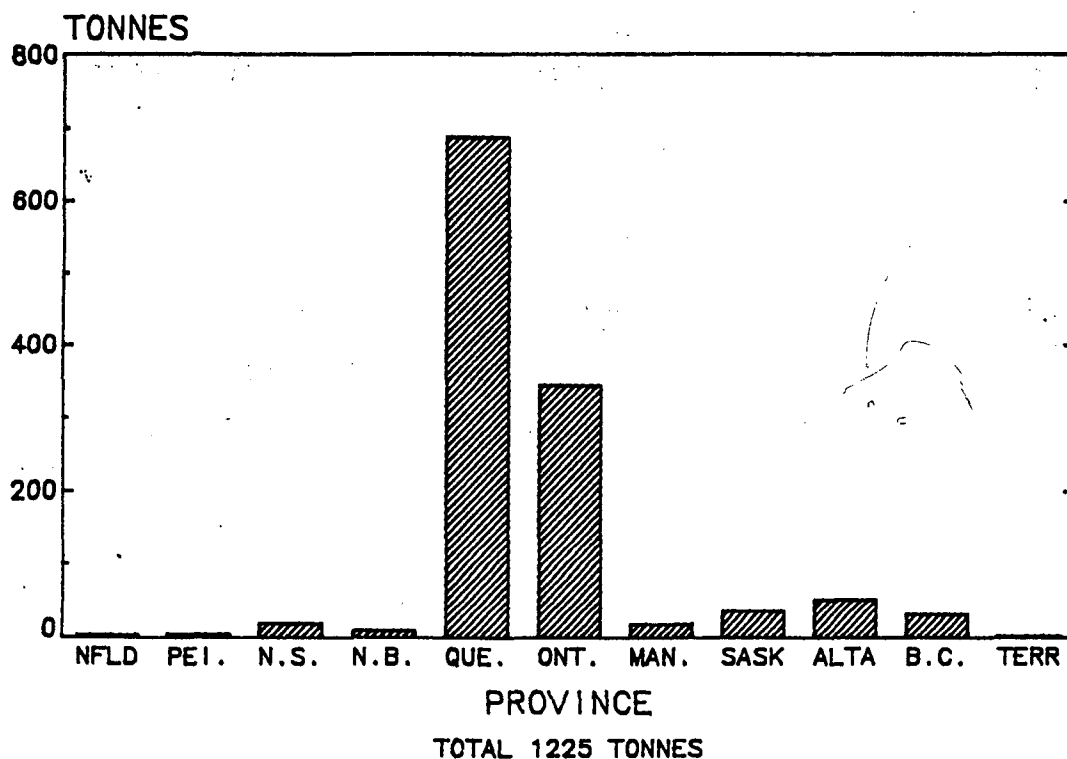[b]   Totals by province do not include pesticide application.

X

TONNES

PROVINCE

TOTAL 1225 TONNES

FIGURE S.1   MANGANESE EMISSIONS BY PROVINCE (1984)

MANGANESE-BEARING ALLOY PRODUCTION

47.0%

MISCELLANEOUS SOURCES

2.3%

OTHER INDUSTRIES

3.9%

0.4%

SOLID WASTE INCINERATION

17.2%

GASOLINE COMBUSTION

1.6%

FUEL COMBUSTION - STATIONARY SOURCES

27.5%

IRON & STEEL PRODUCTION
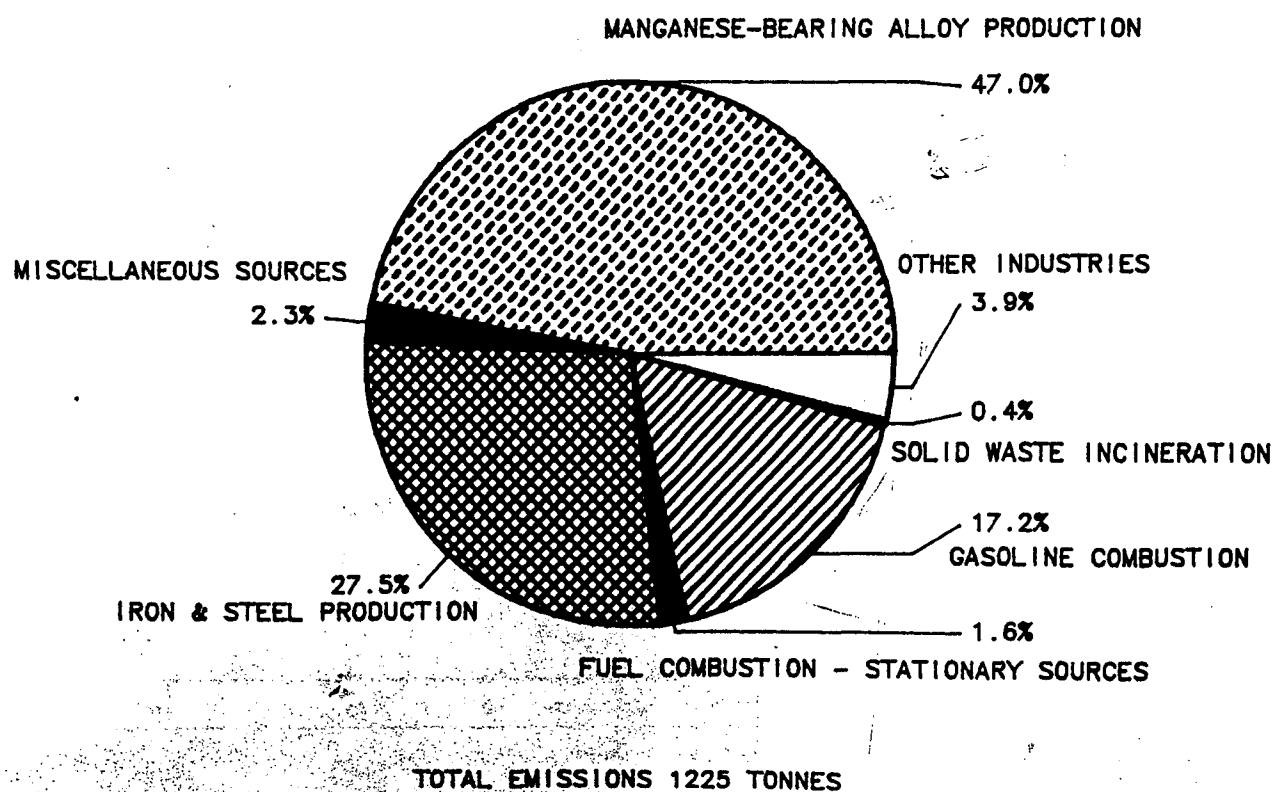
TOTAL EMISSIONS 1225 TONNES

FIGURE S.2   MANGANESE EMISSIONS BY SECTOR (1984)

`1

1   INTRODUCTION

The purpose of this report is to identify and quantify anthropogenic sources of atmospheric emissions of manganese (Mn) in Canada for the year 1984. Information contained in this report was obtained from numerous sources, including: published reports, questionnaires, and personal communication with industry. Where data were available, emissions have been estimated for 1985.

The many industrial processes and activities that generate significant releases of manganese have been described to facilitate the preparation of future inventories and to provide an understanding of the processes involved.
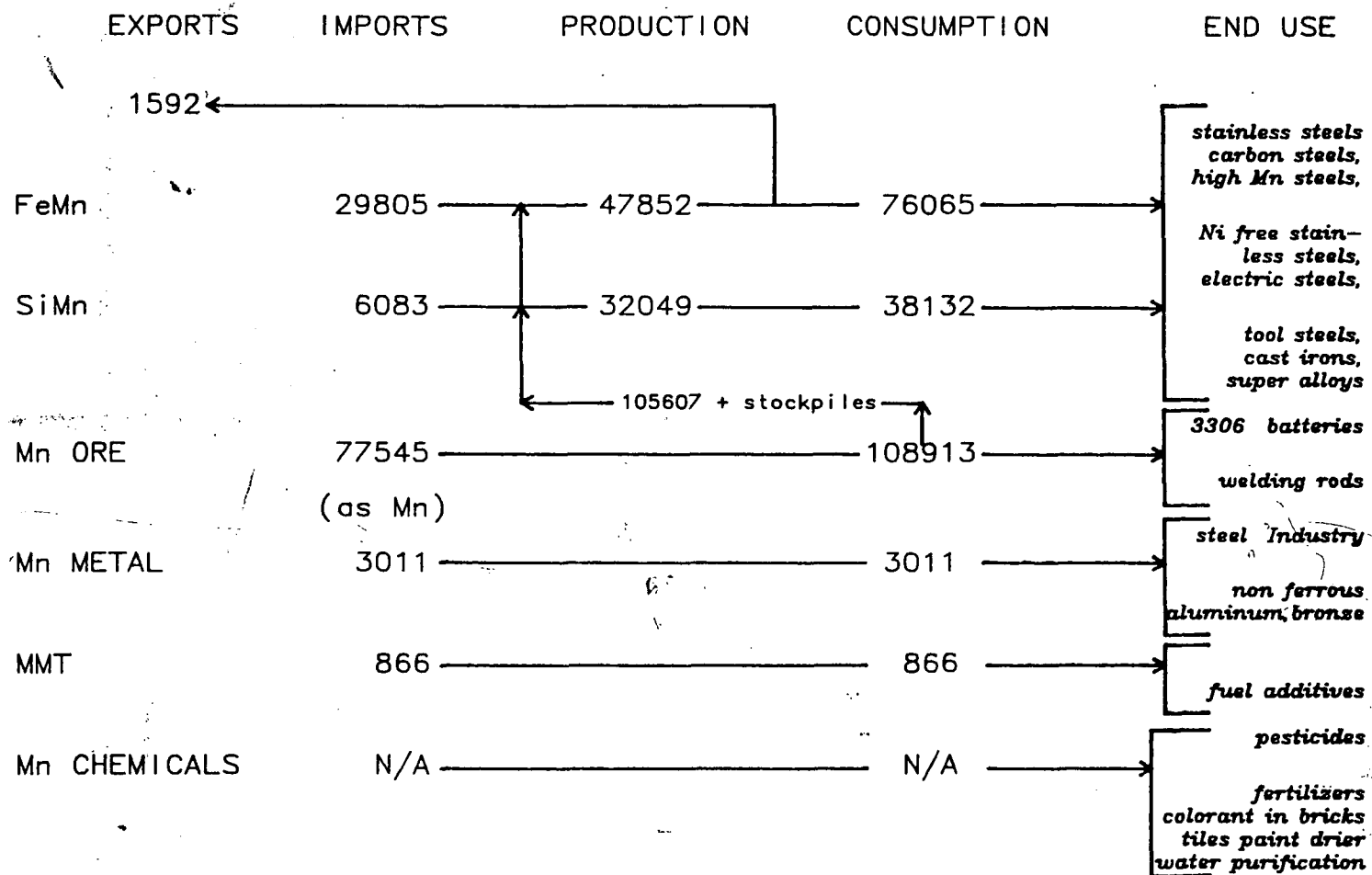
Although manganese is released in various compound forms, all estimates have been expressed as tonnes of elemental manganese.

1.1   Sources and Uses of Manganese

Canada does not mine manganese ore because known deposits contain insufficient tonnage of adequate quality, which makes the country entirely dependent upon imports for the manufacture of manganese products. In 1984, Canada imported 77 545 tonnes of manganese (as elemental manganese) in ores and concentrates, 29 805 tonnes of ferromanganese (FeMn) and 6083 tonnes of silicomanganese (SiMn) (1). Only high carbon ferromanganese, silicomanganese and a few secondary manganese chemicals are manufactured in Canada (2). The consumption of manganese is shown in Figure 1.

Manganese ranks twelfth as one of the more abundant elements in the earth's crust but does not occur as a free metal. The most abundant compounds occur as oxides, sulphides, carbonates and silicates widely distributed in soils, sediments, rocks, water and biological materials. The average concentration of manganese in the earth's crust is approximately 1000 ppm (3,4,5).

Manganese is a hard, brittle, greyish-white metal. Although manganese just precedes iron in the periodic table, it is not ferromagnetic like iron; however, some of its alloys and compounds are. Table 1 presents the physical constants and properties of manganese (6,7). The most important valence states of manganese are $^+2$, $^+4$, and $^+7$, as exhibited in manganese oxide (MnO), manganese dioxide (MnO_2) and permanganate (MnO_4^-), respectively. Some selected manganese compounds are presented in Table 2.

EXPORTS	IMPORTS	PRODUCTION	CONSUMPTION	END USE

1592

FeMn 29805 — 47852 — 76065 →

stainless steels
carbon steels,
high Mn steels,

Ni free stain-
less steels,
electric steels,

SiMn 6083 — 32049 — 38132 →

tool steels,
cast irons,
super alloys

105607 + stockpiles

Mn ORE 77545 — 108913 →

3306 batteries

welding rods

(as Mn)

Mn METAL 3011 — 3011 →

steel Industry

non ferrous
aluminum, bronze

MMT 866 — 866 →

fuel additives

pesticides

Mn CHEMICALS N/A — N/A →

fertilizers
colorant in bricks
tiles paint drier
water purification

Note: quantities are expressed in tonnes.

FIGURE 1   SOURCES AND USES OF MANGANESE (1984)

2

3

TABLE 1   PHYSICAL PROPERTIES OF METALLIC MANGANESE (6,7)

Property	Value
Atomic Number	25
Atomic Weight	54.938
Crystal Structure	cubic or tetragonal
Valence State	-3,1,2,3,4,5,6,7
Melting Point	$1244 \pm 3°C$
Boiling Point	1962 °C
Specific Gravity	7.21 to 7.44
Specific Heat at 25.2°C	0.48 J/g
Linear Coefficient of Thermal expansion 0 to 100°C	$22.8 \times 10^{-6}/°C$
Hardness, Mohs Scale	5
Compressibility	8.4×10^{-7}
Solidification Shrinkage	1.7 %
Standard Electrode Potential	1.134
Magnetic Susceptibility	$1.21 \times 10^{-7} m^3/kg$
Latent Heat of Fusion	244 J/g
Latent Heat of Vapourization	4020 J/g
Solubility	decomposes in water; is soluble in slightly dilute acid

The major sources of man-made environmental pollution from manganese arise in the manufacture of alloys, steel and iron products. Other sources include the combustion of fuel additives, mining of Mn-ores, the production and use of fertilizers and fungicides, and the production of synthetic manganese oxide and dry-cell batteries.

The principal use of manganese is in the production of iron and steel. It is essential to the production of virtually all steels and it is important to the production of cast irons. The principal purpose for adding manganese to steel (as ferromanganese) is to nullify the harmful effects of sulphur by forming manganese sulphide (MnS). It also acts as a deoxidizer and imparts the alloying effects of strength, toughness, hardness, and hardenability. Silicomanganese is used as the alloy feed stock when both silicon and manganese are desired in the steel. The most common grades of steel contain about 0.5 to 1% manganese; however, various specialty steels can contain up to 10%.

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TABLE 2   FORMULAE AND MANGANESE CONTENT OF SOME MANGANESE CHEMICALS (2)

		Manganese (%)	Main End Uses
Manganese acetate tetrahydrate	$Mn(C_2H_3O_2)_2.4H_2O$	25	- oxidation catalyst
Manganese borate	MnB_4O_7		- ink drier, fire-retardant
Manganese carbonate	$MnCO_3$		- natural or intermediate product in making manganese chloride, electrolytic manganese dioxide (EMD) and manganese metal; glass and ceramics; welding rods
Manganese chloride	$MnCl_2$		- glass and ceramics, other chemicals
Manganese ethylene-bisdithiocarbamate (Maneb)	$(CH_2NHCa_2)2Mn$		- fungicide
Manganese dioxide	MnO_2		- magnesium metallurgy, glass and ceramics, primary batteries
Manganese gluconate	$Mn(C_6H_{11}O_7)_2.2H_2O$		- vitamins
Manganese napthenate			- paint additive and drier
Manganese oxide	MnO		- animal foods, fertilizer, micronutrients, welding rods
Manganese phosphate	$Mn_3(PO_4)_2.7H_2O$		- rust proofing
Manganese sesquioxide	Mn_2O_3	69	- ferrites, semiconductors, thermisters and electronics parts
Manganese sulphate	$MnSO_4$	27 to 28	- fertilizer micronutrients, other chemicals
Manganic oxide	Mn_3O_4	70.6	- glass and ceramics, welding rods, coating, welding fluxes, electronics
Methylcyclopentadienyl manganese tricarbonyl (MMT)	$CH_3C_5H_4Mn(CO)_3$		- anti-knock additive in gasoline
Potassium permanganate	$KMnO_4$		- saacharine, oxidizing agent, disinfectant, pollution control

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Manganese is present in all foodstuffs, usually at concentrations below 5 mg/kg. Concentrations in certain cereals, nuts and shellfish, however, can be much higher, exceeding 30 mg/kg in some cases (3). Levels in tea leaves may amount to several hundred mg/kg.

Manganese has been found in measurable quantities in practically all air samples of suspended particulate matter. Annual average levels in ambient air in urban and rural areas not significantly influenced by point source emissions vary from 0.01 to 0.07 $\mu g/m^3$ (2). In areas associated with the manganese industry, however, annual averages have occasionally exceeded 8 $\mu g/m^3$ (3). About 80% of the manganese in suspended particulate matter is associated with particles having a mass median equivalent diameter of less than 5 μm (ie., particles within the respirable range) (3).

1.2 Manganese and Health

Manganese is an essential trace element for both animals and humans. It is necessary for: the formation of connective tissue and bone, growth, carbohydrate and lipid metabolism, the embryonic development of the inner ear, and reproductive functions (3). Food is the major source of manganese for man and the daily requirement for adults is estimated to be 2 to 3 $\mu g/d$.

The daily intake of manganese in the air by the general population in areas without manganese emitting industries, is below 2 $\mu g/d$. In areas with major foundries, intake may rise to 4 to 6 $\mu g/d$ and in areas associated with ferro- or silicomanganese industries it may be as high as 10 μg, with 24-hour peak values exceeding 200 $\mu g/d$ (3).

A health assessment document (8), prepared by the U.S. Environmental Protection Agency (EPA), summarizes the findings of numerous studies concerning the toxicity of manganese. The reader is referred to this document as well as to the Environmental Health Committee's (of EPA's Science Advisory Board) comments for more detailed information.

There are two organomanganese compounds of toxicological importance: manganese ethylene-bis-dithiocarbonate (Maneb) and manganese tricarbonyl compounds. Maneb is used as a fungicide on edible crops. Toxicologically, the manganese fraction is of little importance, it is the organic portion that is of greater concern (3). Manganese tricarbonyl compounds are used as additives in gasoline. After combustion, only a small fraction of the compound is emitted and undergoes rapid photodecomposition, converting to manganese oxides and carbonates. The World Health Organization (WHO) concluded

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that exposure to manganese tricarbonyl compounds is likely to constitute an occupational hazard. Community exposure to the parent compound, however, is expected to remain very small. The WHO recommended that epidemiological surveys be conducted in communities exposed to annual mean concentrations of manganese in air exceeding $1 \mu g/m^3$ (3).

1.3   Methodology

Several methods have been used to estimate emissions of manganese. Emissions were estimated based on data provided by individual companies, surveys and calculations performed by Environment Canada, as well as monitoring data taken from similar processes and emission factors reported in the literature. The emission factor is a statistical average of the rate at which a contaminant is released to the environment, as a result of some activity. It can apply to part of a process or the whole process; with or without emission controls.

The sources of all emission factors presented in this report have been cited. Because most of the emission factors have been developed for materials that contain manganese, the manganese emissions will depend both on the amount of material emitted and the manganese content of the material. This can have a significant effect on estimates. For example, emissions from coal combustion depend on the type of coal and manganese content of the coal which can vary from 6 to 240 ppm.

In compiling any emission inventory, accurate data on the quantity and characteristics of releases from all sources are required. Although the most accurate means of determining releases is monitoring on a source-by-source basis at the point of release, this is made impractical by the large number and diversity of the sources of manganese. Every effort has been made to ensure that the most accurate and recent data available have been used in this report.

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2   INDUSTRIAL EMISSIONS

2.1   Manganese-bearing Alloy Production

In 1984, the reported consumption of metallurgical grades of Mn ores by the two ferromanganese and silicomanganese producers was 222 205 tonnes (9). Since Canada has no domestic producers of manganese ore all of this ore was imported (1). The production of ferromanganese and silicomanganese for 1984 amounted to 47 852 tonnes, and 32 049 tonnes, respectively (9).
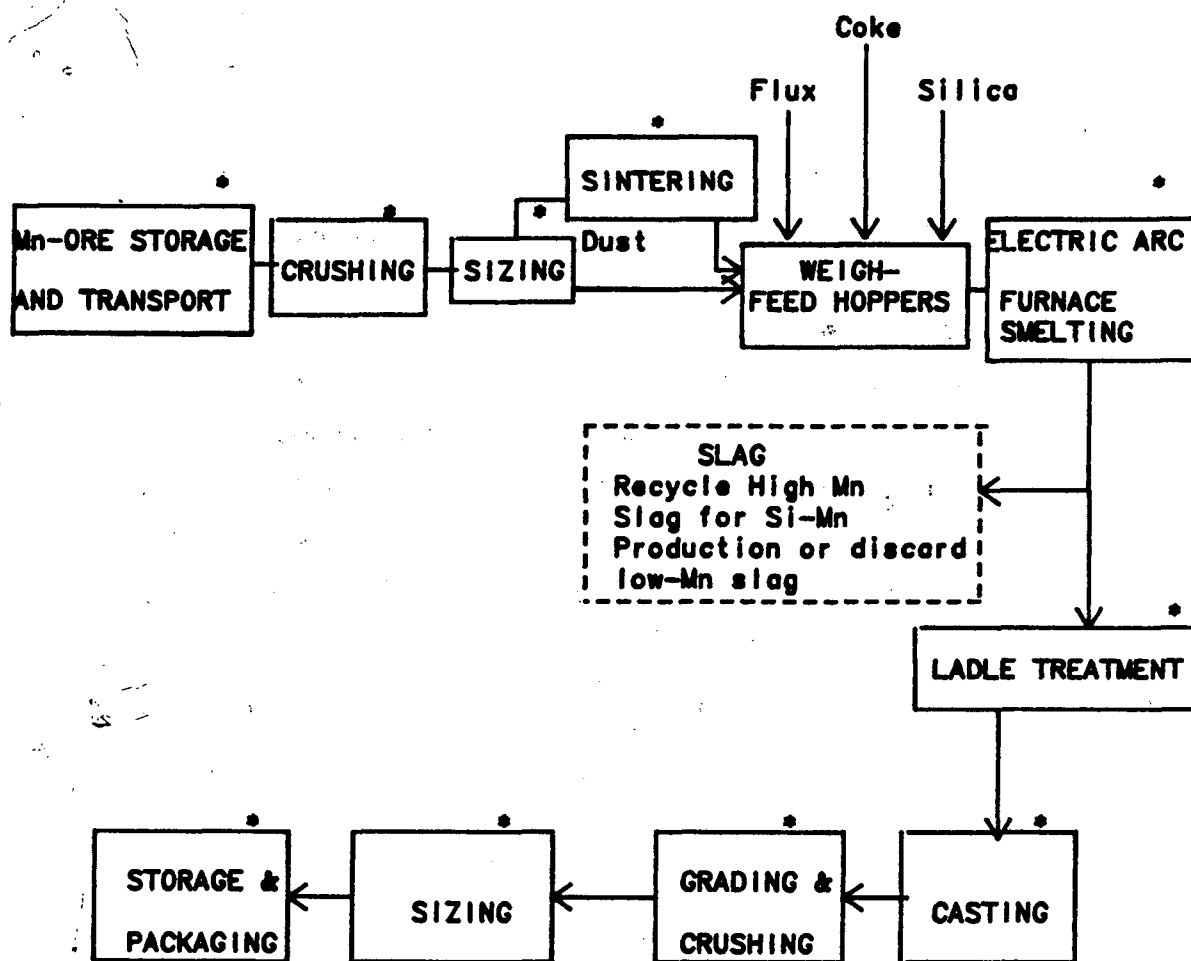
Process Description. Ferromanganese and silicomanganese may be produced in either a blast furnace or an electric furnace. In Canada, all manganese ferroalloys are produced by electric arc furnaces, either sealed or open-top (9).

The electric submerged-arc furnace consists of a refractory-lined hearth and a water-cooled steel shell. Complete oxide reduction is accomplished with intense heat (2200°C to 2760°C). A taphole is provided for draining metal and slag. Normally, three electrodes extend 1 to 1.5 metres into the charge materials. Manganese ore, coke or coal, iron filings, limestone and/or quartz, mixed in proper proportions constitute the charge.

Three-phase current passes through the charge materials from electrode to electrode, and the electrical energy smelts the charge. Coke and other reducing materials that are added to the furnace react with the oxygen in the metal oxides to form carbon monoxide, particulate matter, and metal vapours. The slag is water-cooled and processed. If it has a high manganese content, it is crushed and recycled in the production of silicomanganese; otherwise, it is discarded.

Since a large supply of electric power is necessary for economical operation, the plants are usually located near inexpensive sources of electricity. Submerged-arc furnaces generally operate continuously except for periods of power interruption or mechanical breakdown.

Emission Sources and Controls. The possible sources of manganese emissions from the production of manganese ferroalloys by the electric arc furnace process are shown in Figure 2. Fugitive emissions of manganese occur during the crushing, transfer and stockpiling of manganese-bearing ores and as a result of wind erosion of the stockpiles. The emissions from handling operations are in the form of Mn-bearing particulate. Emissions from storage piles can be reduced by erecting wind barriers, covering the piles with plastic or spraying them with water (7). The extent of these practices is unknown.

8

Coke

Flux   Silica

SINTERING

Mn-ORE STORAGE
AND TRANSPORT → CRUSHING → SIZING → Dust → WEIGH-FEED HOPPERS → ELECTRIC ARC FURNACE SMELTING

SLAG
Recycle High Mn
Slag for Si-Mn
Production or discard
low-Mn slag

LADLE TREATMENT

STORAGE & PACKAGING ← SIZING ← GRADING & CRUSHING ← CASTING

● MANGANESE EMISSION SOURCES
SOURCE: EPA (7)

FIGURE 2   MANGANESE-BEARING FERROALLOYS PRODUCTION BY ELECTRIC ARC FURNACE PROCESS

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The smelting of Mn ore and other raw materials in the electric arc furnace is the major source of Mn-bearing particulate. Open furnaces generate the highest level of emissions because the large opening between the furnace rim and hood allows more circulation of air and gases through the charge, which entrains Mn and particulate.. Fabric filters are used to control emissions from this type of furnace. Testing of these control systems has indicated a total particulate removal efficiency of over 99% (10) although the reported efficiency on this furnace in Canada is 98% (11).

Because minimal air enters sealed furnaces, gas volumes to the control device are only 2 to 5% of those from open furnaces. High-pressure-drop venturi scrubbers are commonly used on this type of furnace with reported efficiencies as high as 99% (11). Additional manganese emissions occur during casting and finishing operations, and the final crushing, sizing and packaging of the ferroalloy products. These operations may be controlled by fabric filters or scrubbers (12).

Emissions. Emissions have been estimated using published emission factors (Table 3). Estimates of fugitive emissions have been generated by the use of predictive equations developed for open dust sources at iron and steel mills (7). Several assumptions have been made in order to develop appropriate emission factors. It was assumed that particulate emission factors for general ferroalloy production also apply to the production of Mn ferroalloys. In order to derive Mn emission factors from total particulate emission factors it was assumed that metallurgical-grade Mn ore contains an average of 45% Mn by weight. The composition of Mn in ferroalloys can range from 75 to 90% in ferromanganese to 63 to 68% in silicomanganese. The Mn emission factors were obtained by multiplying average total particulate emissions from finishing and handling by 80 and 65% for ferromanganese and silicomanganese, respectively.

Based on consumption and production figures, the appropriate emission controls and applicable emission factors, emissions of manganese for 1984 from the ferroalloy industry were estimated to be 576 tonnes (1, 7, 9). Emissions were also estimated for 1985 and due to increased production they were estimated to be 900 tonnes.

2.2 Primary Copper and Nickel Production

There were six primary copper smelters in Canada in 1984, two of which also produced primary nickel. One other smelter produced the remainder of the primary nickel. In 1984, 504 252 tonnes of recoverable copper and 173 725 tonnes of nickel were produced in Canada (13, 14).

TABLE 3   MANGANESE EMISSION FACTORS FROM FERROALLOY INDUSTRY
               (7)

Source		Mn Emission factor
Processing of Raw Materials:		(kg/tonne of ore processed)
Receipt and storage of Mn ore		0.45
Crushing and sizing		0.45
Weighing and feeding		0.40
Smelting in Submerged Arc Electric Furnaces:		
Uncontrolled Sources:	Furnace Type:	(kg/tonne of product)
FeMn	Open	6.6
FeMn	Semi-sealed	2.6
FeMn	Sealed	9.6
Mn	NA	5.7
SiMn	NA	23.2
Controlled Sources:		
FeMn	Open (fabric filter)	0.2
FeMn	Semi-sealed (scrubbers)	0.04
FeMn	Sealed (scrubbers)	0.0038*
SiMn	Open (fabric filter)	0.05*
SiMn	Semi-sealed (scrubbers)	0.016
SiMn	Sealed (scrubbers)	0.001*

Finishing Operations:	FeMn	SiMn
Ladle Treatment	3.75	3.0
Casting	0.24	0.12
Crushing/grinding/sizing	0.08	0.065

*   emission factor in kg/MWh; NA – not applicable

   Process Description. The first step in the production of copper and nickel
involves the concentration of low-grade sulphide ores by magnetic separation and/or

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flotation. The primary metals are then recovered from the concentrate either by roasting, smelting, converting and fire-refining, or by using some of the newly developed pyrometallurgical techniques.

In roasting the concentrates, about half the sulphur is driven off as sulphur dioxide and some of the iron is oxidized. The charge is then melted, usually in a reverberatory furnace, where it separates into an iron silicate slag and a solution of molten sulphides (matte). The mattes are converted through a series of chemical reactions to form the crude metals. The crude copper or nickel is then cast into anodes to be refined by electrolysis.

. **Emission Sources and Controls.** The main atmospheric emission points from the production of primary copper and nickel are the roasters, furnaces, and converters. Emissions from operations such as ore handling and anode furnace are negligible by comparison.

Electrostatic precipitators are used to control particulate emissions from the gases from the roaster, smelting furnace and converter. Baghouses are used for further cleaning of the combined reverberatory furnace and converter gas streams.

Emissions. Data on emissions of manganese from copper and nickel production are almost non-existent. Questionnaire replies have indicated some and estimates have been made based on particulate emissions.

Due to the lack of data, emissions of manganese from copper and nickel production have not been estimated in this report.

2.3 Primary Zinc Production

In 1984, 683 156 tonnes of primary zinc were produced in Canada by four plants.. All the primary zinc in Canada is produced by the electrolytic process, which involves the roasting of the concentrate to drive off the sulphur and obtain oxidized zinc. The roasted ore is termed calcine and contains up to 3% sulphur. The reduction and recovery of zinc is achieved by leaching the calcine with sulphuric acid. The insoluble portion, which contains iron, is separated from the soluble portion and contains about 20% zinc as ferrite in the conventional process and 3% zinc using the "Jarosite Process". Manganese dioxide is added in the leaching process to oxidize the iron. The solution is then purified and sent to cooling towers before going to the electrolysis plant where zinc is plated onto cathodes. The zinc cathodes are then melted and cast into ingots.

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Emission Sources and Controls. The main sources of emissions are the roasters and electrolytic cells. All companies except one have acid plants for the production of sulphuric acid from roaster gases. In addition, the gases prior to entering the acid plant, are cleaned by cyclones, electrostatic precipitators or acid scrubbers, in order to remove particulate matter.

Emissions. Information from questionnaires indicates that concentrations of manganese in the ores range from 0.10% to 0.22% (11). However, no accurate information on the loss of manganese from primary zinc production exists. A recent survey done in the United States does not mention loss of manganese from this type of operation (7).

Due to the lack of accurate data, emissions of manganese from primary zinc production have not been estimated but are considered minor.

2.4 Primary Iron and Steel Production

Iron and steel manufacturing processes include coke production, pig iron manufacture in blast furnaces, steel making using open-hearth, basic oxygen and electric arc furnaces, rolling mill operations and finishing operations. In 1984, the Canadian Steel Industry produced approximately 14.6 million tonnes of crude steel (13).

Molten iron for steel production is obtained by reducing iron ore Fe_2O_3 or Fe_3O_4 to iron in the blast furnace. Preheated air is introduced at high velocity and reacts with the iron ore, coke and limestone. The molten iron is then transported to a steel mill or cast into pigs. The flue dust and other iron ore fines from the process are converted into charge material through sintering. Sinter is an agglomerated product of a size and strength suitable for blast furnace charging. The charge materials, consisting of suitable proportions of iron ore fines, blast furnace (BF) flue dust, mill scale, return sinter fines, limestone fines and coke breeze are mixed with controlled amounts of water and fed to a pug mill or to a balling drum. Here the mixture is ignited in order to cause surface melting and agglomeration of the mix.

In the open hearth (OH) furnace, steel is produced from a charge of scrap and hot metal mixed in varying proportions and melted. Only one company is still using the OH furnace to produce steel.

The basic oxygen furnace and the electric arc furnace accounted for the majority of steel production in 1985. In the basic oxygen process, pure oxygen is used to oxidize impurities in a charge composed of approximately 70% blast furnace metal and 30% scrap metal. The oxidation generates the required heat to melt all the scrap

charged. Lime is added to the vessel to form a slag that contains oxidized impurities from the hot metal and scrap.

The electric arc furnace is a refractory-lined steel cylinder with a bowl-shaped hearth and dome-shaped removable roof. Three carbon electrodes extend through holes in the roof to reach the charge in the furnace. In stainless steel production, the molten steel is transferred from the electric furnace to an Argon Oxygen Deoxidation (AOD) vessel similar to the basic oxygen furnace (BOF). Argon and oxygen and/or nitrogen are blown into the steel for preferential removal of carbon instead of oxidation of chromium (7).

Emission Sources and Controls. All of the materials generated in an integrated steel plant contain some manganese; consequently, blast furnaces, sinter plants, open hearths, basic oxygen furnaces, and electric arc furnaces are the main sources of manganese emissions.

Manganese-bearing emissions occur during storage and during the transfer of iron ore, sinter and pellets to the blast furnace. Emissions also occur during the tapping and transfer of metal and slag within the casthouse. Conditions known as "slips" can cause emissions from the emergency pressure-release valves on top of the furnace (7). Primary emission control devices on the furnace are usually wet scrubbers with secondary cleaning being provided by electrostatic precipitators.

In the sintering process emissions occur from the windbox exhaust, the discharge (sinter crusher and hot screen), the cooler and the cold screens. Mechanical collectors are typically used for product recovery and initial cleaning of windbox exhaust. Secondary collectors may be electrostatic precipitators (ESPs), fabric filters, scrubbers and gravel bed filters (16).

Sources of fugitive emissions from open hearth furnaces include charging, leakage from the furnace, tapping and slag drainage. Controls for fugitive emissions are limited. Emissions from OH furnaces are generally controlled with ESPs or wet scrubbers.

The primary emissions from basic oxygen furnaces are controlled by venturi scrubbers and electrostatic precipitators. Emissions also occur during the transfer of hot metal from the ladle cars to the ladles, the charging of scrap and hot metal to the BOF vessel, slag dumping and tapping of the steel. Secondary controls used to control the charging and tapping emissions may evacuate emissions to a separate fabric filter or to the primary emission control system.

Electric arc furnace emissions occur during periods when the furnace roof is closed (process) and when the roof is open (fugitive). Process emissions consist of

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metallic and mineral oxide particulate as well as some carbon monoxide and hydrocarbons. Charging emissions may contain particulate, carbon monoxide, hydrocarbon vapours, and soot. Fabric filters are the most widely used control devices (17).

Emissions. Emissions have been estimated based on published emission factors (Table 4). Calculations of manganese emission factors are based on the elemental Mn content of the particulate emissions even though most of the manganese emissions are in the form of oxides. It was assumed that the Mn content from the hot metal runners in the blast furnace operations was the same as the Mn content of the dust from the fabric filter controlling hot metal transfer. Further assumptions are noted in Table 4.

. Based on the appropriate emission factors for each plant, furnace type and controls, and the production of iron and steel, total emissions for 1984 were estimated at 337 tonnes (7, 17, 18).

2.5   Iron and Steel Foundries

Scrap iron and steel are melted in different types of furnaces and cast in molds, usually made of sand. Cupola, electric induction, electric arc and reverberatory are the furnace types normally used. The cupola is the major furnace used in a gray iron foundry. It is typically a vertical, refractory-lined, steel shell, which is charged at the top with alternate layers of pig iron, coke and flux. The larger cupolas are water cooled. Air for combustion of coke is introduced at the bottom and the heat generated melts the charge. Hot blast cupolas use preheated air. Cupolas can be tapped either continuously or intermittently from a side tap hole at the bottom of the furnace.

Electric arc furnaces used in foundries are the same as those used in integrated steel plants. Induction furnaces are vertical refractory-lined cylinders surrounded by electrical coils energized with alternating current. The resulting fluctuating magnetic field heats and melts the metal. Induction furnaces remain closed except during charging, skimming and tapping operations. The basic melting process operations are:

1) furnace charging, in which metal, scrap, alloys, carbon and flux are added to the furnace;
2) melting;
3) backcharging;
4) refining;
5) slag removal; and by tapping into a ladle or directly into molds (Figure 3).

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TABLE 4   MANGANESE EMISSION FACTORS FROM IRON AND STEEL PRODUCTION

Type of Operation	Source	Control Device	Product Emission Factor (kg/Mg)
Blast Furnace	Slips	- uncontrolled	0.1185/slip[a]
	Casthouse	- uncontrolled	0.0009[b]
		- runner covers	0.0009
Sintering	Windbox	- uncontrolled	0.067[c]
		- dry ESP	0.0096
		- wet ESP	0.001
		- scrubber	0.0028
		- cyclone	0.006
	Sinter Discharge	- uncontrolled	0.04
		- fabric filter	0.0006
		- orifice scrubber	0.0035
	Windbox and Discharge	- fabric filter	0.0018
Open Hearth Furnace	Melting and Refining	- uncontrolled	0.039[d]
		- ESP	0.0005
	Roof Monitor	- uncontrolled	0.0003
	Teeming	- uncontrolled	0.00013
		- side draft-hood to fabric filter	0.000003
Basic Oxygen Furnace	Top-blown BOF	- uncontrolled	0.1425[e]
	Melting and Refining	- open hood to ESP	0.0065
		- open hood to scrubber	0.00034
	Charging	- at source and monitor	0.00371
	Tapping	- at source and monitor	0.00605
	Hot Metal Transfer	- at source and monitor	0.00027[f]
Electric Arc Furnace	Melting and Refining Charging, Tapping and Slagging	- uncontrolled	0.665[g]
		- uncontrolled	0.0245
	Melting, Refining Charging, Tapping and Slagging	- uncontrolled	0.875
	Carbon Steel	- DEC plus charging hood to fabric filter	0.00075
	Alloy Steel	- uncontrolled	0.328[h]
		- fabric filter	0.0087

a   Mn content of flue dust = 0.3%
b   Mn content of slagrunner fumes = 0.2%; Mn content = 0.4% from hot metal
c   Mn content of sinter = 1.2%
d   Mn content of ESP dust = 0.37%; most of Mn emissions are in the form of oxides
e   Mn content = 1% of the BOF dust and sludge
f   Mn content = 0.26%; based on reladling baghouse dust analysis
g   Mn content of EAF dust - carbon steel, 3.48%
h   Mn content of EAF dust - low and medium alloy 5.76%.
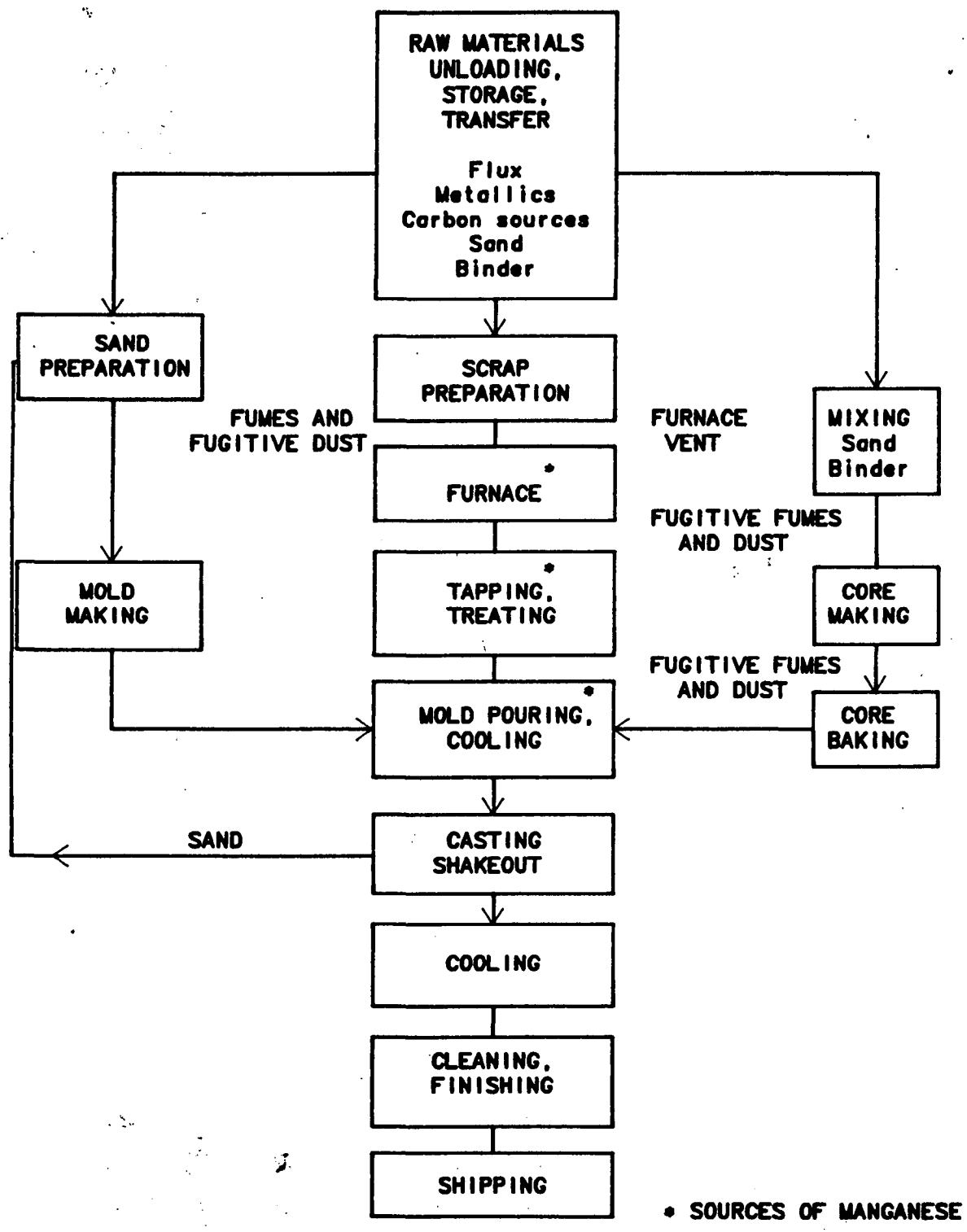
FIGURE 3   GENERALIZED FLOW DIAGRAM OF IRON/STEEL FOUNDRY (6)

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Molten metal is then tapped into a holding unit or into a ladle for pouring into molds. Steel castings are usually cleaned by shot-blasting prior to finishing.

Emission Sources and Controls. Particulate emissions can occur during all of the operations mentioned. The highest concentration of furnace emissions occurs during charging, backcharging, alloying, slag removal and tapping operations. Emissions generated during the melting and refining operations are vented directly to collection and control systems, where they exist.

Emissions consist of metallic oxides, fumes, dust and gases. A large amount of particulate matter is also generated by non-melting operations such as shake-out, shot blasting and sand conditioning. The major emission source is the cupola furnace, with electric arc, induction and reverberatory furnaces emitting smaller amounts.

Emissions from cupolas are controlled by cyclones, fabric filters, wetcaps and scrubbers. Collector units such as baghouses and scrubbers are used in electric arc furnaces. Induction furnaces are usually uncontrolled (7). A variety of hoods, and ventilating and exhaust systems are also employed to capture exhaust foundry emissions.

Emissions. The emissions have been estimated for 1984 based on published emission factors (7, 20, 21) and available information on iron and steel foundries. The calculated emission factors for manganese, which are based on the Mn content in the particulate matter, are presented in Table 5.

Approximately 864 543 tonnes of iron castings and 131 365 tonnes of steel castings were produced in Canada in 1984 (19, 20, 21). Provincial emissions were estimated based on known emission controls, furnace types, and production figures (21, 22). Total manganese emissions for 1984 were estimated to be 40 tonnes.

2.6 . Battery Manufacturing

Manganese dioxide is used as a depolarizer in the manufacture of manganese alkaline batteries. The cathode in these dry cells, is manganese dioxide (MnO_2) with about 10 to 30% carbon (by weight) added to improve conductivity. The collector for the cathode is usually either a carbon rod or a metal rod coated with carbon and the anode is usually the zinc can or zinc sheet. The electrolyte used is generally either a saturated solution of ammonium chloride (NH_4Cl), sodium hydroxide (NaOH) or potassium hydroxide (KOH).

Batteries that use a saturated solution of ammonium chloride as the electro-lyte are known as Leclanché cells. The batteries that use NaOH or KOH as the

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TABLE 5   MANGANESE EMISSION FACTORS FOR IRON AND STEEL FOUNDRIES

Source	Control Equipment	Emission Factor (kg/tonne of product)
Iron Foundries:		
Cupola	- uncontrolled	0.13
	- wet Cap	0.06
	- impingement scrubber	0.0375
	- high energy scrubber	0.006
	- fabric filter	0.0015
Electric Arc Furnace	- uncontrolled	0.075
	- fabric filter	0.00075
Induction Furnace	- uncontrolled	0.01125
Steel Foundries:		
Electric Arc Furnace	- uncontrolled	0.26
	- ESP	0.013
	- venturi scrubber	0.0065
	- fabric filter	0.0004
Induction	- uncontrolled	0.002

electrolyte are known as alkaline cells. Except for the electrolyte used, the MnO_2-zinc cell and the Leclanché cells are essentially the same, although the alkaline cells generally perform better.

Emission Sources and Controls. The Mn ore or synthetic oxides used in the manufacture of dry cell batteries are generally received in bags already ground to the required sizes. The bags are stored, covered with plastic covers and are manually dumped into storage hoppers. In the subsequent steps, the MnO_2 powder is combined with the electrolyte and the rest of the process is conducted under semi-wet conditions.

The only emission sources are at the points of initial handling of the Mn-Ore an MnO_2 powders. In the case of natural ores, grinding and screening may be done at these points, depending on the onsite facilities. These points are generally well controlled by the use of hoods evacuated to fabric filters.

Emissions. Manganese emissions from battery manufacturing have been estimated based on the amount of ore processed and the appropriate emission factors

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shown in table 6 (1, 7). The assumptions made in deriving the emission factors are based on a 50% Mn content in the ore and a 63.2% Mn content in pure MnO_2.

In 1984, approximately 3306 tonnes of battery grade Mn ore (85+% MnO_2) were consumed in Canada (1). Total emissions for 1984 were estimated at 585 kg.

TABLE 6   MANGANESE EMISSION FACTORS IN BATTERY MANUFACTURING

Source	Control Equipment	Manganese Emission Factor (kg/tonne of material handled)
Ore Grinding	- uncontrolled	15.0
	- fabric filter	0.015
Screening	- uncontrolled	0.5
	- fabric filter	0.0005
Storage and Handling	- uncontrolled	2.2
	- fabric filter	0.0022

2.7   Cement Manufacturing

Two methods are used for cement manufacture. In the dry method, feed materials are sent to the process as dry solids. In the wet method, feed materials are mixed with water and sent to the process as a slurry. The raw materials used to make cement fall into four basic categories: lime, silica, alumina and iron. Approximately 1600 kg of dry raw materials are required to produce one tonne of cement (7). Regardless of the type of process used, the materials are proportioned, ground and blended before the primary cement production steps are begun.

In the dry process, the moisture content of the raw material is reduced to less than 1% either before or during the grinding operation. The dried materials are ground to a powder, blended to the prescribed proportion and fed directly into an inclined rotary kiln. In the wet process, the slurry formed by adding water to the original raw materials is blended, mixed, and adjusted to achieve the proper composition. This mixture is then fed to the kilns.

In the kilns slurry and dry raw materials are burned to form clinker, which is then blended with a small amount of gypsum, ground into fine powder and stored.

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Emission Sources and Controls. Cement production is a potential source of manganese emissions because manganese can be a component of the raw materials and because manganese-containing fuels (coal and oil) are burned in the process kilns and dryers.

Manganese emissions consist largely of manganese containing particulate originating from the raw materials, and to a lesser extent from fuel combustion. The major source of emissions is the rotary kiln with lesser amounts being emitted from the grinding mills and the clinker cooler. In the initial grinding stage, emissions are higher at dry-process plants than at wet-process plants. The most common control devices used are electrostatic precipitators for kiln exhaust gases and baghouses for grinding operations.

Emissions. Few direct measurements of manganese emissions from cement plants have been made; however, total particulate emissions from each stage of the process have been reported and the manganese content of emissions has also been measured (7). Manganese emission factors were developed by multiplying particulate factors by the percentage of manganese in particulate emissions, which was 0.05% (Table 7) (7).

TABLE 7   MANGANESE EMISSION FACTORS FOR CEMENT PLANTS

Emission Source	Control	Mn Emission Factor (kg/kt of cement produced)
Dry Process Kilns	– uncontrolled	61
	– ESP	0.0105 to 0.0625
	– fabric filter	0.0065 to 0.062
Dryers and Grinders	– uncontrolled	24
Wet Process Kilns	– uncontrolled	57
	– ESP	0.01 to 0.071
		0.0245 to 0.066
Dryers and Grinders	– uncontrolled	8
Clinker Cooler	– fabric filter	0.0025 to 0.03
	– gravel bed	0.011 to 0.022
	– wet scrubber	0.011

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In 1984, Canada produced approximately 9.2×10^6 tonnes of portland and masonry cement (23). Based on the emission factors, the appropriate control technologies and the production of cement, emissions were estimated at 7 tonnes for 1984.

2.8 Metallurgical Coke Manufacturing

Coke is formed by subjecting low sulphur, low ash coals to indirect heating in long, thin ovens called batteries for 14.5 to 17 hours. The heat drives off the volatile constituents of coal such as benzene and napthalene. Most of the volatile constituents are condensed and recovered as by-products and gas. The hot residue, known as coke, is water quenched and dried.

In 1984, Canada consumed 6.5 million tonnes of metallurgical coal and produced 4.9 million tonnes of coke (24). About 95% of the coke produced in Canada is manufactured via the by-product process.

Emission Sources and Controls. Emissions from coke making are attributable to handling, crushing and blending of coals, charging of coal in incandescent ovens, quenching of hot coke and handling and screening of coke. It is assumed though that most of the manganese contained in coal is volatilized during coking and removed where they exist, in the scrubbing/cooling towers. Therefore, manganese emissions to the atmosphere mainly occur during coal handling operations.

Emissions. Several assumptions have been made in estimating emissions. Since the coal handling operations are low-temperature processes, the content of the particulate emissions should be similar to that of coal. It has been reported (25) that approximately 0.75 kg of particulates are emitted to the atmosphere per tonne of coke produced and the manganese content of appalachian coals range from 5-55 ppm (7). Total emissions from coke manufacturing in 1984 are estimated at less than one tonne.

2.9 Welding Rods

Some welding rods and coatings contain manganese. Aluminum welding rods contain about 1.5% manganese and coatings of other rods contain about 10% manganese. Manganese is added to aluminum welding rods as a general purpose alloy.

To make aluminum welding rods, aluminum-rich alloy ingot containing the manganese is added to a charge of aluminum and alloy scrap in a reverberatory furnace (at 760°C). After melting, the material flows to a trough and is tapped and poured into ingots. The ingots are cooled, and then reheated and rolled in a blooming mill. The product is sent to a rod mill and finished by forging, swaging or draw benching.

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Emissions occur during the melting operation that produces the core and also from the drying and baking of the fluxes on the rods.

Information on the quantity of manganese consumed in welding rod production was not available. However, emissions were estimated at less than one tonne based on industry controls, an uncontrolled emission factor of 8 kg/tonne of Mn processed, production of welding rods and proration of manganese used in welding rods in the United States (26).

2.10 Nonferrous Alloy Industry

Manganese is alloyed with nonferrous metals such as aluminum, magnesium, copper and zinc, and copper and nickel. Manganese is used to make ship propellers, as well as copper-based electrical resistance alloys. Bronze, produced from manganese alloyed with copper and zinc, contains up to 4% manganese. In smaller proportions it is added to corrosion-resisting aluminum alloys and to welding-rod coatings or flux cores (2). Nickel-aluminum bronzes containing 1.5% manganese are being used in some marine applications in place of manganese bronze.

In 1984, approximately 45% of the Mn metal imports (1355 tonnes) were consumed by the nonferrous alloy industries, primarily the aluminum alloy producers (1). Emissions of manganese from the nonferrous alloy industry were estimated at less than one tonne for 1984. This figure was derived based on an uncontrolled emission factor of 6 kg/tonne of Mn processed and the appropriate emission controls in the aluminum industry (26).

2.11 Miscellaneous Sources

2.11.1 Manganese Metal. Emissions of manganese during the production of manganese metal result from the handling, grinding, and roasting of the Mn ore. Since all the manganese metal consumed in Canada is imported (1) and the production of Mn metals is zero, no emissions of manganese are attributable to this industry.

2.11.2 Chemicals. Manganese ore, mainly the dioxide form is used in the chemical industry as an oxidizing agent in the production of hydroquinone, potassium permanganate, manganese sulphate, manganese chloride, manganese oxides and others (26). Emissions do result from these industries; however, Statistics Canada and Energy, Mines and Resources do not report the manufacture of any manganese chemicals in Canada (2, 27, 28). Emissions for chemical production, therefore, are estimated to be zero.

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2.11.3 **Others.** Manganese and its compounds are also used in the production of fertilizers, animal and poultry feed, pharmaceuticals, brits, glass, ceramics, colouring effects to face bricks, paint driers, oxidants and ferrites used in magnets. These chemicals are also employed in air pollution control and in water treatment (26). No data were available on the use of these chemicals in Canada. Emissions from their use have been estimated where information was available.

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3 EMISSIONS FROM FUEL COMBUSTION – STATIONARY SOURCES

3.1 Power Generation

In 1985, electricity generated by coal-fired stations accounted for 54.6% of total thermal generation; oil-fired, 4.9%; natural gas, 1.3%; and nuclear, 39.2%. Hydro-powered generation accounted for 67.1% of the total generation of 446 413 GWh (29).

Two basic systems are used to generate thermal power from fossil fuels: steam generation and internal combustion (gas turbine and reciprocating engines). Steam turbine boilers are fired with coal, heavy fuel oil, crude oil or natural gas (initial steam may be raised by light fuel oil, natural gas, kerosene or diesel oil), whereas reciprocating engines use light oil, natural gas, a combination of both or diesel oil.

Emission Sources and Controls. Manganese emissions from combustion proces-ses depend on the manganese content of the fuel fired, the distribution of manganese between boiler fly ash and bottom ash and the manganese content of the fine fly ash. Manganese is found only in light oils, heavy oils and coal (7).

Manganese concentrations in North American coals range from 3.8 to 526 ppm (30, 31). Manganese concentrations in crude oil are much lower, ranging from 0.005 to 1.45 ppm and averaging 0.21 ppm for U.S. crude oils (26). The manganese content in residual fuel oils averages about 0.16 ppm and 0.01 ppm for distillate oil (7).

The fate of trace elements from the combustion process can be classified by one of three categories:

1)   approximately equal distribution between fly ash and bottom ash;

2)   preferential distribution in the fly ash; and

3)   discharge to the atmosphere primarily as vapours.

Generally, manganese emissions from coal combustion fall under Category 1; however, studies have shown Category 2 behaviour when cold-side precipitators are used (7). Manganese emissions from oil combustion generally fall into Category 2, primarily because little bottom ash is formed in the oil combustion process. The size distribution of manganese concentrations in the fly ash is an important consideration because this determines the efficiency of particulate capture.

All the large coal-fired generating stations are equipped with electrostatic precipitators for particulate control. Efficiencies range from 94.2% to 99%. Cyclones of 70% efficiency are used at some and one station uses a high efficiency fabric filter (32).

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Emissions. Emissions from coal-fired stations were estimated based on the type and consumption of coal by the individual stations (33, 34), the manganese content associated with the type of coal consumed (35, 36, 37), actual source testing data and emissions from four Canadian power plants (38), and emission factors developed from the literature (7). A summary of emission factors for coal and oil fired utility boilers is given in Table 8. It should be noted that these emission factors are general and as such they may not apply to every station.

TABLE 8   EMISSION FACTORS FOR MANGANESE FROM COAL AND OIL
            COMBUSTION: UTILITY BOILERS

Fuel type	Furnace type	Control device	Manganese emission factor (pg/J)
Bituminous coal	- pulverized, dry-bottom	- electrostatic precipitator	41.3
		- scrubber	48.2
		- none	98.0
	- pulverized, wet-bottom	- electrostatic precipitator	33.5
	- cyclone	- electrostatic precipitator	26.1
		- scrubber	54.2
		- none	98.0
	- stoker	- multicyclones	47.3
Anthracite coal	- pulverized	- electrostatic precipitator	41.3
	- stoker	- multicyclones	47.3
Lignite coal	- pulverized, dry-bottom	- electrostatic precipitator	18.1
	- pulverized wet-bottom	- electrostatic precipitator	14.7
	- cyclone	- electrostatic precipitator	57.2
		- multicyclones	711
	- stoker	- multicyclones	47.3
Residual oil	- tangential	- electrostatic precipitator	2.2
		- none	11.0
	- wall	- electrostatic precipitator	2.2
		none	11.0

For oil-fired stations, emissions were based on the fuel consumed, the energy content of the fuel, the appropriate boiler type and the corresponding emission factor (32, 33). Manganese emissions from power generation in 1984 were estimated to be 14 tonnes.

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3.2 Industrial Fuel Combustion

In 1984, approximately 1 615 000 tonnes of coal, 3 789 000 m^3 of heavy oil, and 685 000 m^3 of light oil were used for industrial purposes (33).

Manganese is present in emissions resulting from the combustion of fuels at industrial facilities. The types of fuels used that contain manganese and their corresponding emission factors are presented in Table 9. Based on these emission factors (7), the quantity of fuels consumed (34) and the appropriate energy content, manganese emissions for 1984 from fossil-fuel fired industrial boilers were estimated to be three tonnes.

TABLE 9   EMISSION FACTORS FOR MANGANESE FROM COAL AND OIL
           COMBUSTION: INDUSTRIAL BOILERS

Fuel Type	Furnace Type	Control Device	Manganese Emission Factor pg/J
Bituminous Coal	- pulverized	- multicyclones	29.4
		- scrubber	6.3
	- stoker	- multicyclones	47.3
Residual Oil	- tangential	- scrubber	1.3
		- none	6.5
	- wall	- scrubber	1.3
		- none	6.5
Light Oil		- none	.6

3.3 Commercial Fuel Combustion

Approximately 42 000 tonnes of coal, 753 000 m^3 of heavy oil, and 1 631 700 m^3 of light oil were used for commercial purposes in 1984 (33).

The most common fuels used in commercial establishments are heavy oil, light oil, diesel oil, kerosene and a small amount of coal. Of these only heavy oil, light oil and coal contain manganese (Table 10).

Emissions of manganese from commercial institutions for 1984 were estimated to be 340 kg, based on the amount of fuels consumed and the appropriate emission factors.

TABLE 10   EMISSION FACTORS FOR MANGANESE FROM COAL AND OIL COMBUSTION: COMMERCIAL BOILERS

| Fuel Type	Furnace Type	Control Device	Mn Emission Factor (pg/J)
Bituminous Coal	stoker	none	111
Residual Oil	all	none	6.5
Distillate Oil	all	none	0.6

3.4   Residential Fuel Combustion

In Canada in 1984, approximately 152 000 tonnes of coal, 89 100 m^3 of heavy oil, and 4 893 000 m^3 of light oil were used by domestic dwellings (33).

Fuel consumption figures for heavy fuel oil, light fuel oil and coal (33) along with the appropriate emission factors found in the literature (7) were used to estimate emissions of manganese for 1984 at 3 tonnes. The emission factors presented in Table 11 are based on available information and should only be used as guidelines; emissions from specific sources may vary considerably. A breakdown by fuel type from fuel combustion at stationary sources is shown in Figure 4.

TABLE 11   EMISSION FACTORS FOR MANGANESE FROM COAL AND OIL COMBUSTION: RESIDENTIAL BOILERS

Fuel Type	Furnace Type	Control Device	Mn Emission Factor (pg/J)
Bituminous Coal	all	none	2150
Anthracite Coal	all	none	66.2
Lignite Coal	all	none	430
Distillate Oil	all	none	0.6
Heavy Oil	all	none	6.5

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COAL   HEAVY OIL   LIGHT OIL

TONNES

SECTOR
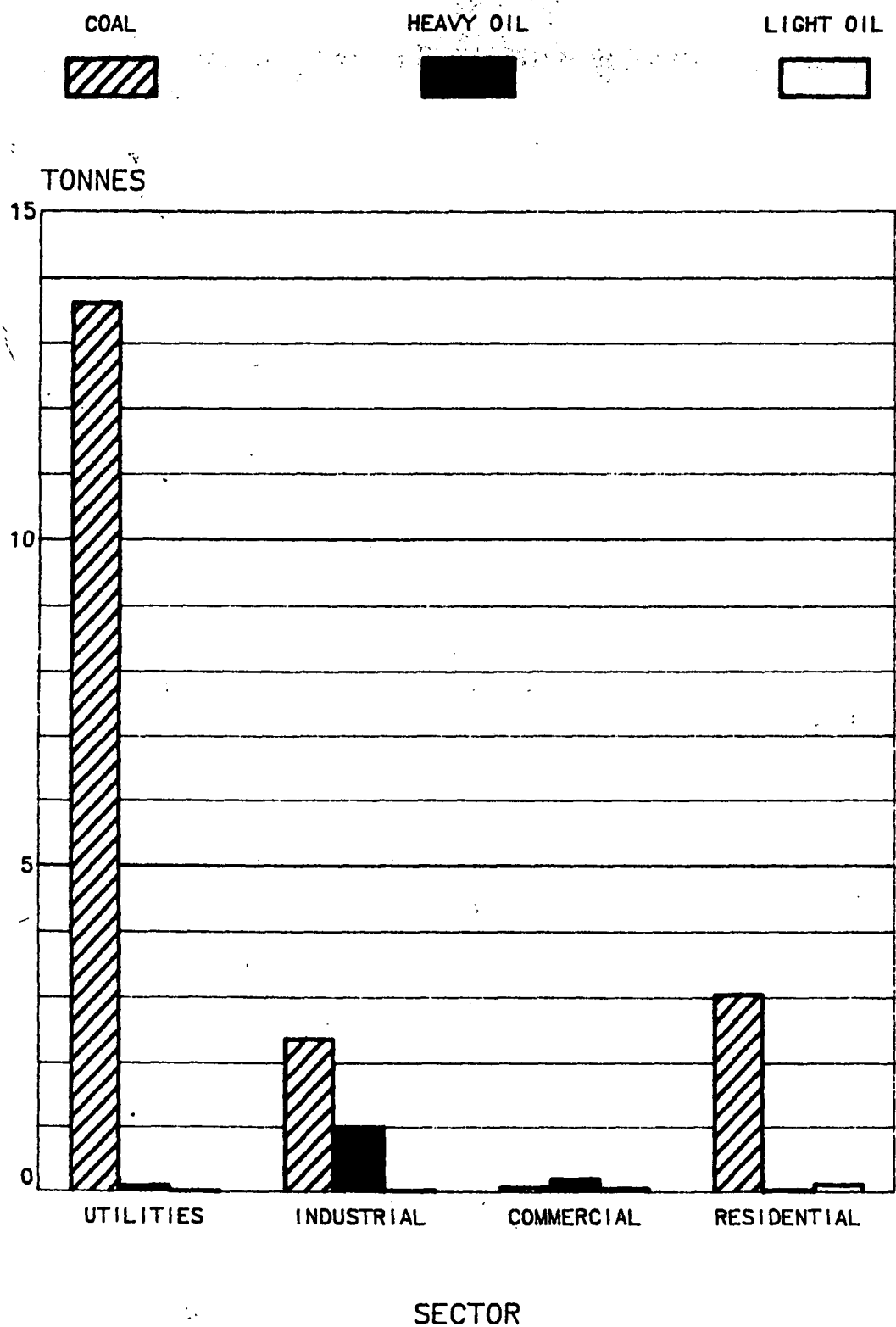
TOTAL 20 TONNES

FIGURE 4   MANGANESE EMISSIONS BY FUEL TYPE FROM FUEL COMBUSTION AT STATIONARY SOURCES (1984)

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4 EMISSIONS FROM FUEL COMBUSTION - TRANSPORTATION SOURCES

4.1 Motor Vehicles and Offroad Use of Gasoline

Emissions from all gasoline-powered vehicles driven on public roads, including automobiles, trucks, buses and motorcycles are covered in this section. Emissions of manganese from gasoline consumption by agricultural, construction and forestry equipment have also been considered.

Gasoline and diesel oil do not normally contain manganese. It is due to the addition of octane enhancers such as Methylcyclopentadienyl Manganese Tricarbonyl (MMT), LP62, and LP46 that gasoline contains manganese. Manganese carbonyls are also used as smoke suppressants in diesel fuels, residual fuel oils and jet fuels.

In 1984, Canada imported additives equivalent to 866 tonnes of MMT (39). The physical properties of MMT and additives are given in Table 12.

4.1.1 Emission Sources and Controls.

Most of the additives (about 99%) are burned along with the fuel and the manganese is converted to the oxide, Mn_3O_4(7, 40). Manganese in unburned and spilled fuel is rapidly converted to manganese oxides and carbonates (7).

Several studies have been made concerning the effects of MMT on emission control devices and emissions. The results of these studies are quite varied (41,42,43). A recent report (43), prepared by a working group of the Canadian General Standards Board Gasoline and Alternate Fuels Committee, in which numerous studies were examined, concludes that the presence of MMT in commercial gasolines has no detectable effect on carbon monoxide or nitrogen oxide emissions. Hydrocarbon (HC) emissions, however, should increase on average from 0.03 to 0.11 g/mile due to the presence of MMT.

The major conclusions in this report were based on two test programs: Co-ordinating Research Council (CRC) study (42) conducted on 63 vehicles in 1977 and 1978; and a 1984 Environment Canada study conducted on 16 Cadillacs equipped with oxidation catalysts in conjunction with three-way catalysts.

The results of the Environment Canada study indicated that these cars would not exceed the proposed hydrocarbon emission level of 0.25 g/km when test results were extrapolated to 80 500 km. Conclusions on hydrocarbon emission increase due to MMT in the gasoline could not be established, however, because no base-line data for similar vehicles operating on clear fuels are available.

TABLE 12   PHYSICAL PROPERTIES OF MMT AND ADDITIVES (39)

MMT ($CH_3C_5H_4Mn(CO)_3$)	MMT	LP62	LP46
Weight % MMT	100	62	46
Weight % Solvent	-	38	54
Volume % MMT	100	50	34
Volume % Solvent	-	50	66
Manganese, wt % (minimum)	24.4	15.13	11.22
Colour	Orange	Orange	Orange
Form	Liquid	Liquid	Liquid
Density at 20°C	0.00138 kg/m^3	0.00111 kg/m^3	0.00702 kg/m^3
Freeze Point (initial)	-1°C	-22°C	-29°C
Flash Point (TCC)	96°C	52°C	48°C
Vapour Pressure at 0°C	5.87 Pa	198.65 Pa	261.31 Pa
Viscosity at 20°C	0.0052 Pa·s	0.0015 Pa·s	0.0012 Pa·s
g/L (elemental Mn/compound)	337	169	115
g/kg (elemental Mn/compound)	224	152	112

The CRC study also concluded that catalyst plugging and spark plug life were not affected by MMT.

On the basis of these results, the working group recommended that MMT be retained at current levels in Canadian unleaded gasoline (43).

4.1.2   **Emissions.** Data are not available on the actual percentage of manganese from MMT that is exhausted. Only about 0.1% of MMT is emitted unburned from the tail pipe (7). Most of the manganese is converted to Mn_3O_4. In Canada, the recommended limit for MMT additives in gasoline is 18 mg Mn/L for both leaded and unleaded fuels. Some provinces have adopted this level in their regulations (44). Based on a manganese content of 24.4% in MMT (45), the amount of MMT imported into Canada and conservatively assuming that all manganese is exhausted to the atmosphere, emissions of Mn for 1984 were estimated to be 211 tonnes. This estimate compares favourably with one made using gasoline sales data for 1984, (46) combined with measured quantities of manganese in leaded and unleaded gasolines (47, 48). Estimates of emissions from the combustion of MMT-containing gasolines for the past few years, are given in Section 7.

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4.2   Aircraft

Aircraft considered in this section have the reciprocating (piston) engine commonly associated with small, light-weight aircraft.

Emissions of manganese were assumed to be zero since no manganese additives were reported in aviation gasoline. The quantities of manganese consumed in jet fuels are unknown and therefore emissions have not been estimated from this source.

4.3   Gasoline Outboard Motors

Emissions to the atmosphere from gasoline outboard motors were not estimated due to insufficient data. However, because the concentration of manganese in leaded gasoline is less than unleaded (48), the quantities of gasoline consumed by marine engines are a small fraction of the total gasoline consumed, and most exhaust from outboard engines is underwater, emissions are considered negligible.

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5   EMISSIONS FROM WASTE INCINERATION

5.1   Municipal Refuse Incineration

Municipal incineration is a process that reduces the volume of solid waste by burning. Some incinerators are best suited for incineration of a waste with particular physical characteristics. Typical municipal refuse incinerators consist of either refractory-lined or water-walled combustion chambers with a grate upon which refuse is burned. The manganese-laden exhaust gases are commonly sent to a control device before being emitted to the atmosphere.

Emission Sources and Controls. Manganese emissions from municipal refuse are a function of:

1)   the manganese concentration of the refuse;

2)   the amount of manganese adsorbed on particulates or volatilized in the gas stream; and

3)   the type of air pollution controls used (49).

The combustion temperature of the incinerator can influence the volatilization of the manganese species and increase emissions. The control systems used on municipal incinerators range from systems that simply reduce gas velocity in settling chambers to sophisticated electrostatic precipitators that remove up to 99% of all particulate matter (49).

Emissions. Emissions were estimated based on the quantity of refuse incinerated by each plant, an emission factor of 0.020 kg/t of waste for uncontrolled emissions (26), 0.005 kg/t of waste for controlled emissions (7) and in the case of the P.E.I. incinerator 0.0011 kg/t of waste (50).

In 1985, approximately 909 000 tonnes of refuse were disposed of in Canadian incinerators. Total manganese emissions from municipal refuse incineration in 1985 were estimated to be 5 tonnes.

5.2   Sewage Sludge Incineration

Sewage sludge is a by-product of sewage treatment processes. In the incineration process, sludge is freed of moisture prior to combustion and the temperature is elevated to the ignition point. Air and auxiliary fuel may be required to support and maintain combustion. The residual inorganic ash is then cooled and disposed of. Multiple-

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hearth furnaces were used at three incineration facilities while fluidized bed incinerators were used at the remainder. The furnace is the major source of particulate emissions.

Emission Sources and Controls. As with municipal refuse incineration, manganese emissions from sewage sludge incineration are a function of the manganese concentration of the sludge, the amount of manganese adsorbed on particulate matter, or volatilized in the gas stream and the air pollution controls used. Concentrations of manganese in municipal sewage vary widely, depending on the sewered industrial population, the mixing of storm and sanitary sewage and the amount of infiltration of material other than sewage sludge (49).

Emissions. Trace amounts of manganese have been found in sewage sludge ranging from 100 to 8800 ppm (7). Based on the quantity of sludge incinerated, emissions were calculated using manganese emission factors given in Table 13.

In 1985, approximately 111 000 tonnes of sewage sludge were incinerated in Canada. Total manganese emissions from sewage sludge incineration in 1985 were estimated to be less than one tonne.

TABLE 13   EMISSION FACTORS FOR MANGANESE FROM MUNICIPAL REFUSE
            AND SEWAGE SLUDGE INCINERATORS

Incinerator Type	Control Device	Mn Emission Factor kg/t of waste incinerated
Municipal Refuse	- none	0.020
Municipal Refuse	- electrostatic precipitators	0.005
Sewage Sludge (multiple-hearth)	- wet scrubber	0.002
Sewage Sludge (fluidized bed)	- wet scrubber	0.0003

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6   EMISSIONS FROM MISCELLANEOUS SOURCES

6.1   Gasoline Marketing

In addition to the inorganic emissions of manganese created by the combustion of gasoline containing MMT, organic manganese emissions may occur during the handling of gasoline. The evaporation of MMT and other manganese carbonyls, however, is probably not a source of significant manganese air emissions.

Commercial MMT is a liquid that solidifies at -1°C and has a boiling point of 233°C (7). The flash point is 96°C and the density is 1.38 g/mL. Typically, gasoline is 90% distilled at 167°C and the dry point is 209°C (51). Therefore, MMT is appreciably less volatile than gasoline.

Since no emission factors have been developed for emissions of manganese due to evaporation, emissions have not been estimated. Because of the low volatility of MMT in comparison with gasoline though, evaporative losses from fuel tanks are not considered a significant source of manganese emissions.

6.2   Pesticide Application

In 1985, approximately 1380 tonnes of Maneb and Mancozeb (manganese-containing pesticides) were sold in Canada. Both pesticides are used as fungicides and are very similar in chemical composition. The only difference is that Mancozeb contains zinc and is a superior fungicide. Their main applications are in the control of specified fungal diseases on turf and vegetables including potatoes and tomatoes as well as the control of a variety of insects and fungal diseases on roses and flowers (52).

When considering the emissions resulting from the use of pesticides it is important to consider all the parameters that determine the percentage 'drift' (i,e., the amount of pesticide that escapes the target area). The factors that affect drift are droplet size of the liquid, wind speed, temperature, foliage, density, humidity, and operator skill.

Pesticide application is dependent upon chemical makeup and desired effect. Losses during aerial application range from 10% to 50% (53). In fruit tree spraying the air emission may be 50% early in the season when the leaves are small but as the leaf cover increases the drift decreases. Other types of application have a loss of about 10%.

Based on a 10% drift loss and a manganese concentration of approximately 20% in Mancozeb (52), emissions from pesticide application for 1985 are estimated to be 28 tonnes.

7   EMISSION TRENDS

The magnitude of manganese emissions depends mainly on three sectors: ferroalloy production, iron and steel production, and gasoline-powered motor vehicles. In 1984 these three sectors accounted for 92% of the total manganese emissions.

This report is the first published report on emissions of manganese in Canada. An earlier study (1972) was commissioned by Environment Canada for internal purposes; however, any comparisons with that study and this, should be made carefully. The 1972 estimates were made assuming no emission controls for either the ferroalloy or the iron and steel industries. Consequently, the emission estimates are several times greater than those given in this report. Emissions from gasoline-powered motor vehicles were estimated as negligible in 1972. It was not until 1976 that MMT first appeared in motor gasolines and 1977 that significant emissions occurred.

The general trend in emissions though, closely follows the activity in the ferroalloy and iron and steel industries, since together these industries accounted for 75% of the total emissions in 1984 and about 80% in 1985. Although the combustion of MMT-containing gasolines contributes a significant proportion of the total emissions of manganese, emissions from this sector have remained relatively constant throughout the 1980s. In fact, although emissions increased by 10 tonnes from 1984 to 1985, the contribution of this sector to the total declined from 17% to 14%.

Figure 5 illustrates the trend in emissions of manganese from the combustion of MMT containing gasolines. These are conservative estimates based on the assumption that all of the manganese contained in the fuel is emitted and on information provided by Ethyl Canada (46).

The maximum possible emissions of manganese from gasoline combustion are estimated to be 518 tonnes. This figure is based on 1985 gasoline production figures and a manganese content of 18 mg Mn/L of gasoline. This is the current limit set by the Canadian General Standards Board. However, emissions are unlikely to reach this level until leaded gasoline is phased out, since current levels of manganese average 3 mg/L and 13 mg/L in leaded and unleaded gasolines, respectively.
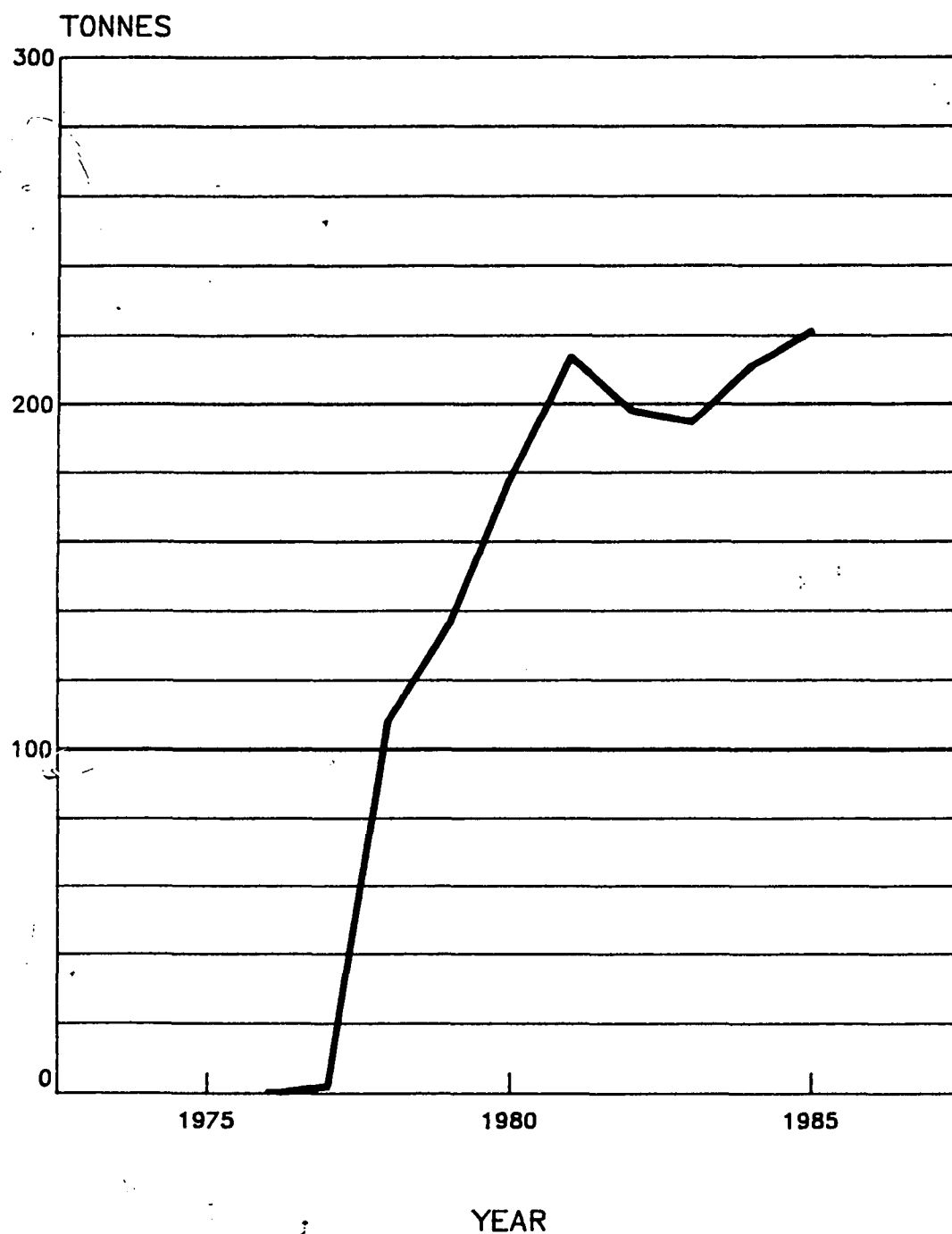
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FIGURE 5 ESTIMATED EMISSIONS OF MANGANESE FROM GASOLINE COMBUSTION (1975-1985)

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Results from

Inhalable Particulate Matter (PM$_{10}$)

Sampling Network (1984 - 1987)

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1. INTRODUCTION

In anticipation of a future revision to the total suspended particulate matter ambient air quality objective for Canada, Environment Canada, in conjunction with provincial and municipal operating agencies, established in June 1981 an inhalable particulate matter monitoring program. Three years of data were gathered at seven urban sites using 15 μm inlet dichotomous samplers; reports summarizing the results of this sampling effort have previously been published.[1,2] In May 1984, the original samplers were converted using 10 μm cutpoint inlets and additional samplers were added to the network. A report summarizing mass, lead, sulphate, nitrate and bromine data collected up to March 1985 was distributed in 1986.[3] This report contains all mass, sulphate and nitrate data for the period May 1984 to December 1987 and data for 40 other elements associated with particulate matter for the period November 1985 to December 1987.

The particulate matter samplers used in this study were designed to have a 50% cutpoint (D_{50}) of 10 μm particle aerodynamic diameter. D_{50} is defined as the particle size at which the sampler collects 50% of the sample and rejects 50%. Particles whose aerodynamic diameters are below the D_{50} of 10 μm are collected at progressively greater than 50% efficiency while those particles larger than D_{50} are collected with progressively less efficiency. Thus, 10 μm particulate samples do contain particles larger than 10 μm. This is consistent, however, with the physiology of the human respiratory system where a large percentage, but not all, of particles larger than 10 μm are trapped in the oral/nasal passage and prevented from entering the lung.[4,5] The mass of particulate collected with a sampler with a 10 μm inlet is referred to as PM_{10}. An alternative name for this particulate mass fraction is inhalable particulate (IP).

2. SAMPLING SITES and SCHEDULES

A list of sampling sites (as of December 1987) and a summary of sampler distances from the ground and from roadways is given in *Table 1*. All sites were located in commercial areas close to or in the central business districts of the respective cities. Only the Sydney site was close to a large industrial point source. The Vancouver site (00118) was relocated in December 1986 and the Regina site was relocated in September 1986. Since the relocation distances were relatively small, the data from the previous and present sites have been combined.

Normally, all samples were collected over a 24h sampling period on a six day sampling schedule. The two Vancouver sites operated on a three-day sampling schedule from January 1985 to December 1987. Ten of the seventeen sites were operational by the end of May 1984; five sites did not begin operation until August 1984 and one site (Victoria) produced no valid PM_{10} data during 1984. The Windsor site began operation in July 1987. Data from St. John's is available only for the period September 1984 to October 1985.

3. METHODOLOGY

3.1 Sampling Equipment

As shown in *Table 1*, fourteen sites were equipped with dichotomous samplers and five sites with size selective hi-vol (SSI) samplers. Two sites, Ottawa and Edmonton, had both SSI and dichotomous samplers.

The dichotomous samplers were manufactured by Sierra-Andersen and divide 10 μm inhalable particulate into two size fractions above and below 2.5 μm (*see Figure 1*). These two fractions are referred to as the *COARSE* and *FINE* fractions respectively. The

FIGURE 1 - SIERRA-ANDERSEN DICHOTOMOUS SAMPLER

SAMPLING MODULE

CONTROL MODULE

40"

22"

16"

25"

AIR FLOW

10 µm FRACTIONATING INLET

FINE PARTICLE TRAJECTORY

ACCELERATION NOZZLE

COARSE PARTICLE TRAJECTORY

FRACTIONATION ZONE

COLLECTION NOZZLE

FINE PARTICLE FILTER

COARSE PARTICLE FILTER

● PARTICULATES <2.5 µm
○ PARTICULATES 25-100 µm

Inhalable Particulate Matter (PM$_{10}$) Sampling Network 1984-87 - PMD 90-3

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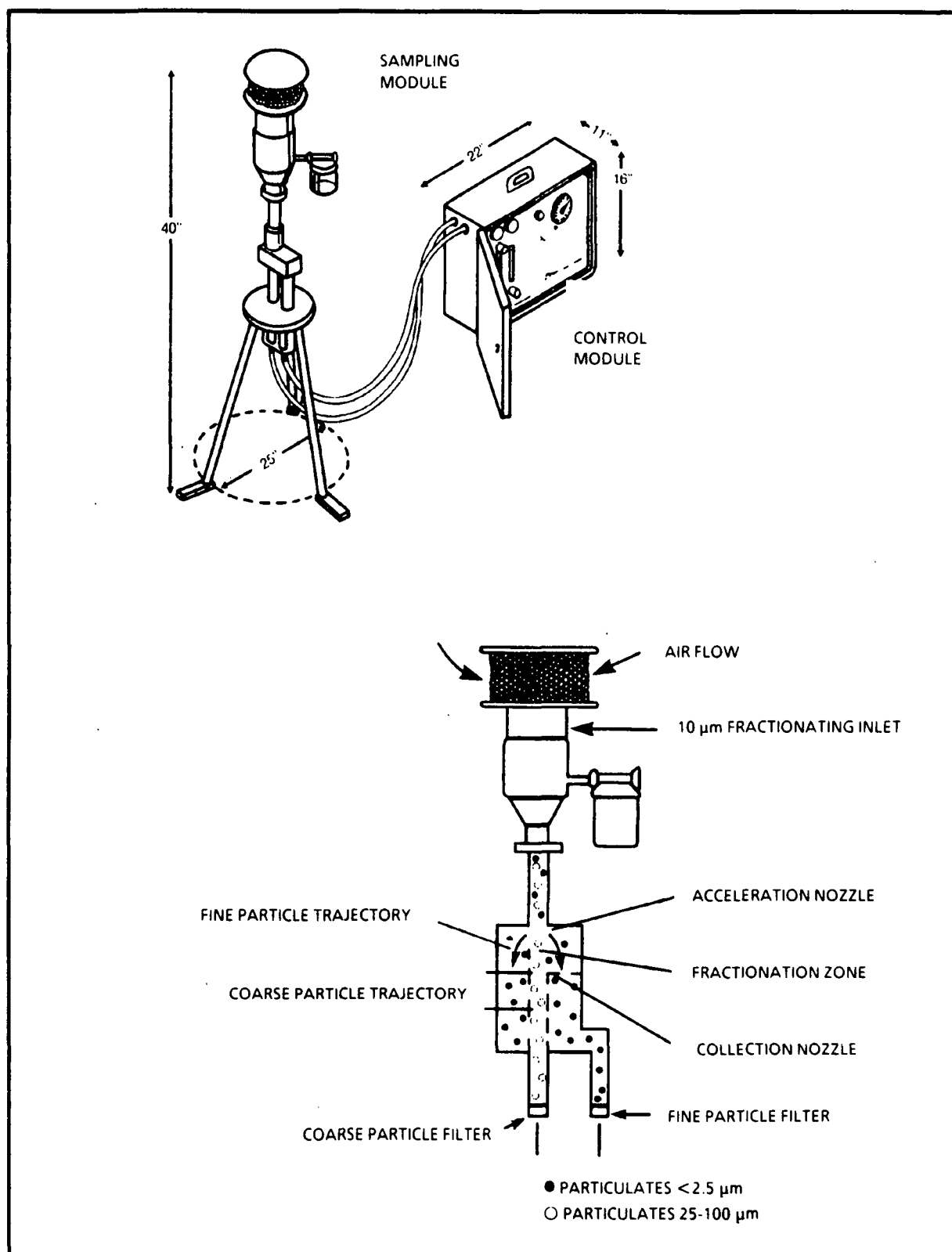
TABLE 1 - INHALABLE PARTICULATE SAMPLING LOCATIONS

Station No.	City	Address	Sampler Type Dichot (D) SSI (S)	Height Above Ground (m)	Distance to Roadway (m)	Roadway ADT (veh/day)
10101	St. John's	Duckworth/Ordinance	D	9	35	<10,000
30101	Halifax	N.S. Technical College	D	12	100	10,000
50104	Montreal	1125 Ontario Est	D	13	10	32,000
50109	Montreal	Duncan/Decarie	D	4	20	>100,000
50307	Quebec City	Parc Cartier Breboeuf	D	4	75	2,500
60104	Ottawa	Rideau/Wurtemburg	D,S	4	80	32,000
60417	Toronto	26 Breadalbane Street	D	16	100	52,000
60204	Windsor	471 University Avenue	D	12	--	--
70119	Winnipeg	65 Ellen Street	D	4	55	14,000
90130	Edmonton	10255-104th Street	D,S	6	5	10,400
90204	Calgary	316-7th Avenue	D	9	25	16,000
00118*	Vancouver	2550 West 10th Avenue	D	17	25	<4,000
00111	Vancouver	Rocky Pt. Park	D	4	300	28,000
00303	Victoria	1250 Quadra St.	D	12	18	12,000
30311	Sydney	Whitney Pier Fire Stn.	S	2	--	--
40201	Saint John	110 Charlotte Street	S	17	10	<10,000
80110+	Regina	3211 Albert Street	S	8	20	50,000

* Relocated from site 00106 in Dec. 86   + Relocated from site 80109 in Sept. 86

samplers were operated at a total flowrate of 16.7 L/min; particulates were collected on Tefweb polyolefin ring-supported Teflon membrane filters manufactured by Ghia Corporation (2 μm effective pore diameter).

The size selective inlet hi-vol samplers utilized a General Metal Works (GMW) base, a Moore and Gentry flow controller and a Sierra-Andersen S/A-321 10 μm inlet. Particulates were collected on Pallflex Emfab Teflon coated glass fibre filters, shown to reduce artifact sulphate and nitrate formation.[1] The operating flowrate was 1.13 m^3/min (40 cfm).

The S/A-321 inlet has been shown to allow large particle pass-through (from bounce and/or re-entrainment)

resulting in an overestimation of PM_{10} concentrations.[6] This overestimation is most significant when coarse particle loadings are high. The inlets on all samplers were replaced in December 1988 with Sierra-Andersen 1200 inlet heads.

Standard hi-vol samplers were also operated at each site in order to provide total suspended particulate (TSP) measurements. All hi-vol samplers, except those in Toronto and Windsor employed low artifact filter media (see Table 2). The sampling effectiveness of the hi-vol is wind dependent with a cutpoint of about 50 μm with 2 km/h winds and about 22 μm with 24 km/h winds.[7] The hi-vols were operated at flowrates of 1.13 to 1.41 m^3/min.

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TABLE 2 - INHALABLE PARTICULATE SAMPLE PROCESSING

Station No.	City	Address	Sampler Type Dichot (D) SSI (S)	Hi-Vol Filter Type	Hi-Vol Mass Determ.	Hi-Vol Pb, SO$_4$, NO$_3$ Determ.
10101	St. John's	Duckworth/Ordinance	D	Pall[1]	PMD	CD
30101	Halifax	N.S. Technical College	D	Pall	NS	CD
50104	Montreal	1125 Ontario Est	D	Gel-A[2]	MUC	MUC
50109	Montreal	Duncan/Decarie	D	Gel-A[2]	MUC	MUC
50307	Quebec City	Parc Cartier Breboeuf	D	Pall	QUE	QUE
60104	Ottawa	Rideau/Wurtemburg	D,S	Pall	PMD	CD
60417	Toronto	26 Breadalbane Street	D	Gel-AE[3]	ONT	ONT
60204	Windsor	471 University Avenue	D	Gel-AE	ONT	ONT
70119	Winnipeg	65 Ellen Street	D	Pall	MAN	MAN
90130	Edmonton	10255-104th Street	D,S	Pall	ALTA	ALTA
90204	Calgary	316-7thAvenue	D	Pall	ALTA	ALTA
00118*	Vancouver	2550 West 10th Avenue	D	Pall	GVRD	CD
00111	Vancouver	Rocky Pt. Park	D	Pall	GVRD	CD
00303	Victoria	1250 Quadra St.	D	Pall	PMD	CD
30311	Sydney	Whitney Pier Fire Stn.	S	Pall	NS	CD
40201	Saint John	110 Charlotte Street	S	Pall	NB	CD
80110+	Regina	3211 Albert Street	S	Pall	PMD	CD

[1] Pallflex Emfab   [2] Gelman A (Pre-washed)   [3] Gelman AE

3.2   Analysis

3.2.1 Mass. All PM$_{10}$ mass determinations (both SSI and dichotomous) were performed by Pollution Measurement Division in Ottawa. Dichotomous sampler filters were shipped to and from the field loaded in plastic rings which were designed to fit directly into the Andersen samplers. The filters, in their rings, were packaged in plastic petri dishes and shipped in a wooden box designed to hold them in an upright position. Mass measurements were made using an electronic microbalance. All filters were conditioned at 25°C and 50% relative humidity prior to mass determination.

3.2.2 Sulphate/Nitrate. All analyses were performed by Chemistry Division (CD) of RRETC, Ottawa. Sulphate and nitrate analyses on dichotomous filter samples (fine and coarse) were performed using a Dionex ion chromatograph equipped with a HPIC-AS4A anion exchange separator column with a carbonate/bicarbonate buffer eluant. Detection was by conductivity with chemical eluant suppression. Filters were extracted with water in an ultrasonic bath.

For SSI filter cuttings, sulphates and nitrate analyses were carried out using an automated Technicon methyl thymol blue method.

As shown in *Table 2*, hi-vol filter cuttings were analyzed either by CD Ottawa or by the respective operating agencies. Sulphate and nitrate

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determinations on hi-vol filter samples processed by Ottawa were made using the Technicon method.

3.2.3 Multi-element Analysis. Lead analyses for SSI filter cuttings and for hi-vol filter cuttings processed in Ottawa were carried out using a wavelength dispersive X-ray fluorescence spectrometer.

Beginning in November 1985, every fifth set of dichotomous filters from each site were submitted for multi-element analysis. As of December 1986, all dichotomous filter samples were analyzed for the list of elements shown in *Table 3*. Multi-element analyses were carried out by CD using a Kevex 770/8000 energy dispersive X-ray fluorescence (EDXRF) spectrometer. Three different measurement conditions were used.

4. QUALITY ASSURANCE

4.1 Samplers

Dichotomous samplers, SSI hi-vols and regular hi-vols were calibrated and operated in the field by the respective provincial or municipal environment agencies. Periodic audits of the samplers were carried out by Environment Canada staff using reference flow control devices. The United States EPA Inhalable Particulate Network Operation and Quality Assurance Manual was used as a guidance document.

4.2 Mass Determinations

A polonium radioactive source was used as a static charge control device when weighing dichotomous, SSI and hi-vol filters. Standard sets of filter were weighed periodically to verify precision and accuracy of the balance. Repeat weighing of exposed filters were carried out on a systematic basis. A dedicated temperature and humidity

controlled room was used to carry out mass determinations.

TABLE 3 - SUMMARY of ELEMENTS on DICHOTOMOUS FILTER SAMPLES

Element	Symbol	Detection Limit (ng/m³)
Aluminum	Al	3.9
Silicon	Si	1.8
Phosphorus	P	0.8
Sulphur	S	0.7
Chlorine	Cl	1.9
Potassium	K	1.8
Calcium	Ca	2.2
Scandium	Sc	2.5
Titanium	Ti	4.9
Vanadium	V	3.9
Chromium	Cr	3.2
Manganese	Mn	2.1
Iron	Fe	2.3
Cobalt	Co	1.4
Nickel	Ni	1.1
Copper	Cu	1.7
Zinc	Zn	1.1
Gallium	Ga	1.2
Germanium	Ge	0.8
Arsenic	As	0.5
Selenium	Se	0.5
Bromine	Br	0.4
Rubidium	Rb	0.3
Strontium	Sr	0.3
Yttrium	Y	0.3
Zirconium	Zr	0.4
Niobium	Nb	0.5
Molybdenum	Mo	0.6
Palladium	Pd	2.4
Silver	Ag	2.6
Cadmium	Cd	3.3
Indium	In	3.5
Tin	Sn	4.3
Antimony	Sb	4.7
Tellurium	Te	4.8
Iodine	I	5.0
Cesium	Cs	8.9
Barium	Ba	11.9
Lanthanum	La	15.5
Lead	Pb	0.8

It should be noted that TSP determinations were made by nine different agencies. No interlaboratory

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comparison of hi-vol mass determinations has been carried out to date.

4.3 Analytical

Complete details of analytical quality assurance procedures will not be included in this report. Information on calibration and quality control techniques for EDXRF and IC analyses is available from CD, Ottawa.

4.4 EPA Reference Method for PM_{10}

The United States EPA has published a reference method for the determination of particulate matter as PM_{10} in the atmosphere.[8] Manufacturers of sampling equipment are required to undergo a rigorous program of laboratory and field testing to obtain certification as a reference or equivalent PM_{10} monitoring method.[8,9] Instruments are required to have a 50% cutpoint of 10 ±0.5 μm aerodynamic diameter and a precision of ±5 μg/m³ for PM_{10} concentrations <80 μg/m³ and ±7% for PM_{10} concentrations >80 μg/m³. The average 24h flow rate must be within ±5% of the initial flowrate. As discussed in Section 3.1, because of large particle pass through problems, the S/A 321 inlet could not pass EPA equivalency certification. The Sierra-Andersen Model 241 dichotomous sampler and the Sierra-Andersen Model 1200 SSI hi-vol have received equivalency certification.[9]

5. RESULTS and DISCUSSIONS

5.1 Air Quality Objectives

A Canadian national ambient air quality objective for PM_{10} has not yet been established. In 1987, the United States did replace their total suspended particulate (TSP) standards with PM_{10} standards as shown in Table 5. The U.S. primary standards are not directly comparable to Canadian air quality objectives. As shown in Table 5,

the original U.S. primary TSP standard was substantially higher than the Canadian maximum acceptable air quality objective.

5.2 PM_{10} Measurements

5.2.1 Mass. The means of the fine (<2.5 μm) and coarse (2.5 to 10 μm) PM_{10} mass fractions and the mean total PM_{10} mass

TABLE 4 - U.S. EPA PM_{10} METHODOLOGY REQUIREMENTS

Filter	
Collection Efficiency:	>99% for 0.3 μm DOP test
Integrity:	blank filter losses/ gains equivalent to 5 μg/m³ of PM_{10} (filter cassette recommended)
Alkalinity:	<25 microequivalents/gm of filter
Filter Conditioning	
Temp.Range:	15° to 30°C
Temp. Control:	±3°C
Humidity Range:	20% to 45% RH
Humidity Control:	±5% RH
Flow Measurement	
Accuracy:	±2%
Calibration:	Reference to primary standard

TABLE 5
TSP and PM_{10} AIR QUALITY STANDARDS
CANADA and the UNITED STATES

Avg. Time	CANADA (Maximun Acceptable Level) TSP (μg/m³)	U.S. (Primary Standard)	
		TSP (μg/m³)*	PM_{10} (μg/m³)
24h	120	260	150
Annual	60[a]	75[a]	50[b]

[a] Geometric mean [b] Arithmetic mean
* Withdrawn in 1987

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concentrations for the dichotomous sampler sites are presented in *Table 6.* Also included are the mean fine/coarse mass ratios and associated standard deviations. For the SSI sites, mean PM_{10} mass loadings are given. As noted in Section 2, the Windsor site did not begin operation until July 1987 and data from St. John's are only available for 1985. For the other sites, the total number of sampling days in the May 1984 to December 1987 period ranged from 131 to 259.

Mean PM_{10} mass concentrations ranged from 17 $\mu g/m^3$ in St. John's to 49 $\mu g/m^3$ at the Montreal Duncan/Decarie monitoring site. Eastern sites tended to have a higher fine fraction of PM_{10} and higher fine/coarse ratios than the western sites. The Montreal Duncan/-Decarie site and the Edmonton site had the highest coarse particulate loadings and the lowest fine/coarse ratios. Only the Montreal Duncan/Decarie site came close to exceeding the U.S. annual average primary standard for PM_{10}.

As previously discussed, the S/A 321 SSI hi-vol inlet has been shown to overcollect coarse particulates result-ing in an overestimation of PM_{10} levels. This error has been shown to be as high as +25% at sites with high coarse loadings.[6] From *Table 6* it can be seen that the mean PM_{10} concentration at Edmonton as recorded by the SSI was 28% higher than that measured by the dichotomous sampler (46 $\mu g/m^3$ vs 36 $\mu g/m^3$). At Ottawa, the SSI mean PM_{10} concentration was essentially the same as that measured by the dichotomous sampler. Coarse particulate loadings at the Ottawa site were approximately half of those at the Edmonton site. Further discussion of SSI/dichotomous sampler differences are contained in Section 5.3.

Table 7 contains a frequency distribution of 24h PM_{10} mass concen-trations for each site. Few 24h PM_{10} concentrations greater than the pro-posed 24h EPA primary standard of 150 $\mu g/m^3$ were recorded. The distribution

of sampling days within selected ranges of PM_{10} mass concentrations is shown in *Table 8.* The Federal Provincial Advisory Committee on Air Quality (FPACAQ) Index Subcommittee has proposed these interim PM_{10} ranges for use with a new index system. Values of 0-50 $\mu g/m^3$ would be characterized as good, 51-100 as fair, 101-150 as poor and >150 $\mu g/m^3$ as very poor.

A comparison of PM_{10} concentrations for selected sites in the United States and Canadian cities is given in *Figure 2.* Plotted are 90th percentile and 50th percentile concentrations. The United States data is for 1986 for the cities of Steubenville, Ohio (STE), Watertown, Massachusetts, (WAT), Topeka, Kansas (TOP) and St. Louis, Missouri (STL).[10] Steubenville is a heavily industrialized city of 26,000, Watertown is a residential, non-industrial suburb of Boston, Topeka is a non-industrial city of 120,000 and St. Louis is an industrialized metropolitan city of 425,000.

5.2.2. Sulphate. A dichotomous sampler equipped with teflon filter media is the preferred sampling system for sulphate in ambient air.[1,11] The teflon coated glass fibre filter used on the SSI hi-vols has been shown to have low sulphate artifact but would be expected to produce somewhat higher particulate sulphate concentrations than a dichotomous sampler at the same site.

Table 9 contains mean fine (<2.5 μm), coarse (2.5 to 10 μm), and total sulphate loadings for the dichotomous sampler sites. Also shown are the mean fine/coarse sulphate ratios and associated standard deviations. For the SSI sites, mean total sulphate loadings are given.

For sites with a complete data set, mean total sulphate concentrations ranged from 5.6 $\mu g/m^3$ at Halifax to 1.7 $\mu g/m^3$ at Edmonton. Sulphate loadings at eastern sites were typically 2 to 3 times higher than loadings at western sites.

Table 6: Mean PM10 Mass Loadings and Fine/Coarse Ratios
(May 1984 - December 1987)

Station Number	City	SSI(S) Dichot(D)	Number of Samples	Mean Coarse (μg/m^3)	Mean Fine (μg/m^3)	Mean Total (μg/m^3)	Mean F/C Ratio	Std. Dev. Ratio
10101	ST. JOHN'S	D	39	7	10	17	1.5	1.0
30101	HALIFAX	D	182	14	16	30	1.3	0.8
30311	SYDNEY	S	199	-	-	34	-	-
40201	SAINT JOHN	S	189	-	-	24	-	-
50104	MONTREAL	D	208	15	20	35	2.1	3.1
50109	MONTREAL	D	168	26	23	49	1.0	0.6
50307	QUEBEC CITY	D	127	11	12	23	1.5	1.6
60104	OTTAWA	D	212	10	13	23	1.7	1.4
60417	TORONTO	D	167	11	17	28	2.0	1.5
60204	WINDSOR	D	22	17	22	39	1.5	0.6
70119	WINNIPEG	D	178	18	13	31	1.1	1.2
80110	REGINA	S	196	-	-	37	-	-
90130	EDMONTON	D	167	21	14	36	0.9	1.0
90204	CALGARY	D	187	18	14	32	1.1	1.2
00118	VANCOUVER	D	182	11	16	27	1.7	1.2
00111	VANCOUVER	D	259	14	17	31	1.5	1.1
00303	VICTORIA	D	131	7	14	21	2.2	1.5
60104	OTTAWA	S	211	-	-	24	-	-
90130	EDMONTON	S	195	-	-	46	-	-

Table 7: Frequency Distribution of PM10 Mass (µg/m³)
(May 1984 - December 1987)

Station	City	SSI(S) Dich(D)	No. of Samples	Frequency Distribution Min.	5	10	20	30	40	50	60	70	80	90	95	98	99	Max.	Mean	Std. Dev.
10101	ST. JOHN'S	D	39	2	3	5	11	12	14	16	19	22	25	29	31	34	34	34	17	8
30101	HALIFAX	D	182	10	14	17	19	21	25	27	31	35	40	49	56	75	81	85	30	14
30311	SYDNEY	S	199	2	9	12	16	21	22	27	31	36	43	61	87	172	192	194	34	30
40201	SAINT JOHN	S	189	0	12	13	15	16	20	22	26	29	32	37	45	57	60	64	24	11
50104	MONTREAL	D	208	9	13	16	20	24	27	30	35	39	47	59	68	82	104	154	35	20
50109	MONTREAL	D	168	12	20	23	30	34	39	42	49	55	68	83	97	116	126	175	49	25
50307	QUEBEC CITY	D	127	6	10	12	13	15	17	19	23	28	33	40	43	57	58	61	23	12
60104	OTTAWA	D	212	5	8	10	13	16	18	20	23	27	33	39	49	59	60	65	23	12
60417	TORONTO	D	167	8	11	12	16	19	22	24	27	32	38	48	51	67	83	91	28	14
60204	WINDSOR	D	22	11	14	17	26	28	28	32	37	40	54	63	92	100	100	100	39	23
70119	WINNIPEG	D	178	6	11	13	17	19	23	25	30	36	40	53	63	95	99	112	31	19
80110	REGINA	S	196	6	10	13	17	23	27	32	40	47	55	69	82	93	98	105	37	22
90130	EDMONTON	D	167	9	15	20	24	28	30	34	37	43	47	54	60	73	84	86	36	14
90204	CALGARY	D	187	4	11	14	17	21	25	29	33	35	41	56	72	82	89	114	32	18
00118	VANCOUVER	D	182	6	12	14	16	19	21	24	27	29	34	50	56	69	84	84	27	14
00111	VANCOUVER	D	259	9	13	15	20	23	26	29	34	38	43	48	56	68	73	82	31	14
00303	VICTORIA	D	131	4	9	10	12	14	16	18	21	23	28	34	44	51	52	59	21	11
60104	OTTAWA	S	211	4	9	10	14	17	19	20	23	27	31	40	52	63	66	80	24	13
90130	EDMONTON	S	195	8	13	19	24	30	35	40	44	49	60	82	112	136	163	185	46	29

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Table 8: Summary of PM10 Concentrations Within Selected Ranges
(May 1984 - December 1987)

Station	City	SSI(S) Dich(D)	Total No. of Days	No. of Days with PM10 Concentration ($\mu g/m^3$)			
				0-50	51-100	101-150	>150
10101	ST. JOHN'S	D	39	39	0	0	0
30101	HALIFAX	D	182	166	16	0	0
30311	SYDNEY	S	199	173	18	3	5
40201	SAINT JOHN	S	189	184	5	0	0
50104	MONTREAL	D	208	174	30	3	1
50109	MONTREAL	D	168	104	57	6	1
50307	QUEBEC CITY	D	127	122	5	0	0
60104	OTTAWA	D	212	204	8	0	0
60417	TORONTO	D	167	158	9	0	0
60204	WINDSOR	D	22	17	5	0	0
70119	WINNIPEG	D	178	157	20	1	0
80110	REGINA	S	196	146	49	1	0
90130	EDMONTON	D	167	147	20	0	0
90204	CALGARY	D	187	163	23	1	0
00118	VANCOUVER	D	182	165	17	0	0
00111	VANCOUVER	D	259	240	19	0	0
00303	VICTORIA	D	131	128	3	0	0
60104	OTTAWA	S	211	200	11	0	0
90130	EDMONTON	S	195	140	44	9	2

Figure 2: Comparison of PM10 Concentrations
Canada - USA

Table 9: Mean SO4 Loadings and Fine/Coarse Ratios
(May 1984 - December 1987)

Station Number	City	SSI(S) Dichot(D)	Number of Samples	Mean Coarse (μg/m³)	Mean Fine (μg/m³)	Mean Total (μg/m³)	Mean F/C Ratio	Std. Dev. Ratio
10101	ST. JOHN'S	D	38	0.4	2.6	3.0	6.8	3.4
30101	HALIFAX	D	189	0.4	5.1	5.6	14.3	15.4
30311	SYDNEY	S	204	-	-	4.1	-	-
40201	SAINT JOHN	S	194	-	-	5.0	-	-
50104	MONTREAL	D	210	0.5	4.1	4.6	16.3	68.8
50109	MONTREAL	D	168	0.6	4.2	4.8	10.1	21.4
50307	QUEBEC CITY	D	149	0.4	2.5	2.8	11.5	35.3
60104	OTTAWA	D	209	0.3	3.7	3.9	19.0	35.8
60417	TORONTO	D	166	0.4	4.5	4.9	12.1	9.9
60204	WINDSOR	D	22	0.5	6.7	7.1	15.8	15.9
70119	WINNIPEG	D	179	0.3	1.6	1.9	6.4	4.3
80110	REGINA	S	201	-	-	2.3	-	-
90130	EDMONTON	D	185	0.3	1.5	1.7	6.5	5.7
90204	CALGARY	D	187	0.3	1.6	1.9	6.1	7.4
00118	VANCOUVER	D	181	0.3	2.2	2.6	7.5	4.2
00111	VANCOUVER	D	253	0.3	2.1	2.4	7.7	4.4
00303	VICTORIA	D	131	1.0	1.9	2.8	6.5	4.1
60104	OTTAWA	S	216	-	-	4.7	-	-
90130	EDMONTON	S	201	-	-	2.7	-	-

As shown in *Table 9*, sulphate is associated predominantly with the fine fraction of particulate matter. Excluding Victoria, coarse sulphate loadings were similar across the country with a range of 0.3 to 0.6 µg/m³. Victoria had the highest coarse sulphate concentrations (1.0 µg/m³); this sulphate probably originates from ocean aerosols.

In *Table 10*, the frequency distribution of 24h total sulphate concentrations for the PM_{10} sampling sites are given. Maximum sulphate concentrations of >25 µg/m³ were measured at the two Montreal sites and at all the Ontario sites.

In *Table 11*, the fine sulphate is given as a fraction of fine particulate mass for each dichotomous sampler site. At the eastern sites, sulphates accounted for 17% to 31% of total fine particulate mass with a median value of 24%. At the western sites, sulphate accounted for 11% to 15% of fine particulate mass.

5.2.3. Nitrate. Because of the volatility of particulate nitrate, losses can occur from filter media during sampling. This effect can be significant for both low volume techniques such as the dichotomous sampler and hi-volume techniques such as the SSI hi-vol. Offsetting this loss, filter media can absorb nitric acid which will be measured by the analytical method as nitrate, resulting in a positive nitrate "artifact".[3,12,13] Nitric acid adsorption would be more significant for the SSI hi-vols than for dichotomous samplers.

The means of the fine, coarse and total nitrate concentrations for the dichotomous samplers are given in *Table 12*. Mean fine/coarse nitrate ratios and associated standard deviations are also given. For the SSI sites, mean total nitrate loadings are shown.

Mean total nitrate loadings ranged from 0.6 to 1.5 µg/m³. As for sulphate, Victoria had the highest coarse nitrate concentration (0.9 µg/m³) of any site. The Toronto and the two Montreal sites had the highest fine particulate nitrate concentrations.

5.2.4 Other Elements. As noted in Section 3.2.3, a subset of filters were submitted for multi-element energy dispersive x-ray fluorescence (EDXRF) analysis. A total of 40 elements in addition to sulphate, nitrate and mass were determined for these samples. *Table 13* provides a summary of the number of samples for each site that were submitted for multi-element analysis. The dates of the samples and the mean PM_{10} mass concentrations of the samples analyzed by EDXRF vs mean PM_{10} concentrations) for all samples for the site are also given. One additional site (Walpole Island) was available for the EDXRF data set. This site is a rural site located on an island in Lake St. Clair.

Mean fine, coarse and total concentrations for each element are given in *Tables A1 to A43* of *Appendix A*. *Tables B1 to B43* of *Appendix B* contain frequency distributions of total elemental concentrations.

Comparisons of concentrations of 15 selected elements by city are given in *Figures 3 to 6*. Crustal elements such as aluminum (Al), silicon (Si), calcium (Ca) and Iron (Fe) are associated with the coarse fraction of PM_{10} and originate primarily from wind blown dust and road dust. Chlorine is also associated with coarse particles and is associated mainly with roadway salting and marine aerosols.

Sulphur comes predominantly from secondary sulphate and, as discussed in the sulphate section, is associated almost entirely with the fine fraction of PM_{10}. There was an excellent correlation between EDXRF sulphur versus ion chromatography sulphate (see *Figure 7*). Based on molecular weight, if

Table 10 : Frequency Distribution of Sulphate (SO4) Concentrations (μg/m³)
(May 1984 - December 1987)

Station	City	SSI(S) Dich(D)	No. of Samples	Frequency Distribution Min.	5	10	20	30	40	50	60	70	80	90	95	98	99	Max.	Mean	Std. Dev.
10101	ST. JOHN'S	D	38	0.0	0.7	1.2	1.5	1.9	2.5	2.7	3.3	4.0	4.6	5.1	5.8	6.4	6.4	6.4	3.0	1.5
30101	HALIFAX	D	189	0.9	1.7	2.1	2.8	3.4	3.9	4.7	5.5	6.4	8.0	10.5	12.0	16.2	18.7	21.7	5.6	3.5
30311	SYDNEY	S	204	1.1	1.5	1.9	2.4	2.7	3.1	3.5	4.0	4.5	5.6	7.0	9.3	10.9	11.3	15.3	4.1	2.3
40201	SAINT JOHN	S	194	0.0	1.7	2.0	2.9	3.4	3.8	4.5	5.1	5.5	6.4	8.4	11.2	13.6	14.6	21.3	5.0	2.9
50104	MONTREAL	D	210	0.3	1.0	1.2	1.7	2.3	2.9	3.5	4.4	5.4	6.8	9.3	12.1	15.4	16.6	28.1	4.6	3.9
50109	MONTREAL	D	168	0.2	1.0	1.3	1.8	2.5	3.1	3.8	4.7	5.3	7.2	10.0	10.8	13.4	17.1	33.3	4.8	3.9
50307	QUEBEC CITY	D	149	0.4	0.5	0.7	1.1	1.4	1.8	2.2	2.7	3.3	4.1	6.4	7.3	8.8	10.0	17.1	2.8	2.3
60104	OTTAWA	D	209	0.0	0.7	1.0	1.3	1.8	2.2	2.8	3.5	4.6	5.4	8.1	11.4	14.1	24.3	29.3	3.9	4.1
60417	TORONTO	D	166	0.1	0.7	1.3	1.7	2.3	3.0	3.6	4.5	5.7	7.4	9.5	13.3	16.1	29.1	40.4	4.9	4.9
60204	WINDSOR	D	22	1.1	1.6	2.6	3.1	3.4	3.8	6.1	6.9	7.7	11.2	12.0	15.4	27.9	27.9	27.9	7.1	6.0
70119	WINNIPEG	D	179	0.0	0.5	0.7	1.0	1.2	1.4	1.6	1.9	2.3	2.8	3.5	4.4	5.0	6.6	6.9	1.9	1.2
80110	REGINA	S	201	0.0	1.0	1.2	1.4	1.6	1.8	2.0	2.3	2.6	3.1	3.5	4.2	5.5	6.0	10.8	2.3	1.2
90130	EDMONTON	D	185	0.0	0.5	0.6	0.8	0.9	1.1	1.3	1.6	1.9	2.4	3.4	4.7	6.8	8.6	12.6	1.7	1.6
90204	CALGARY	D	187	0.3	0.4	0.5	0.7	0.9	1.1	1.3	1.6	1.8	2.2	3.7	5.4	11.4	15.1	18.9	1.9	2.4
00118	VANCOUVER	D	181	0.5	1.0	1.2	1.4	1.6	2.0	2.2	2.5	3.0	3.7	4.5	5.2	6.4	6.8	9.0	2.6	1.4
00111	VANCOUVER	D	253	0.0	0.7	0.9	1.2	1.5	1.7	2.1	2.5	3.0	3.5	4.3	5.0	5.6	6.2	8.5	2.4	1.4
00303	VICTORIA	D	131	0.2	0.9	1.1	1.3	1.5	1.6	1.9	2.1	2.3	3.0	3.7	4.9	6.6	13.4	81.6	2.8	7.1
60104	OTTAWA	S	216	0.1	1.1	1.4	2.0	2.4	3.1	3.8	4.4	5.5	6.6	8.8	12.8	16.7	24.1	25.3	4.7	3.9
90130	EDMONTON	S	201	0.5	0.9	1.1	1.4	1.5	1.8	2.1	2.4	2.8	3.3	4.3	6.6	9.7	10.5	21.9	2.7	2.5

Table 11: Fine Sulphate as a Fraction of Fine Mass at Dichotomous Sampler Sites
(May 1984 - December 1987)

Station Number	City	No. of Samples	Mean Fine SO4 (μg/m³)	Mean Fine Mass (μg/m³)	Mean SO4/Mass Ratio	Std. Dev. Ratio	Maximum Ratio
10101	ST. JOHN'S	37	2.6	10.2	0.24	0.09	0.43
30101	HALIFAX	182	5.1	16.2	0.31	0.11	0.79
50104	MONTREAL	208	4.1	19.7	0.21	0.10	0.60
50109	MONTREAL	167	4.2	23.1	0.17	0.09	0.49
50307	QUEBEC CITY	125	2.3	11.8	0.20	0.12	0.94
60104	OTTAWA	209	3.7	13.2	0.25	0.11	0.64
60417	TORONTO	164	4.5	17.0	0.24	0.11	0.75
60204	WINDSOR	22	6.7	22.5	0.27	0.10	0.45
70119	WINNIPEG	177	1.6	12.7	0.14	0.08	0.39
90130	EDMONTON	170	1.5	14.5	0.11	0.08	0.49
90204	CALGARY	186	1.6	14.0	0.12	0.09	0.56
00118	VANCOUVER	180	2.2	16.3	0.15	0.06	0.37
00111	VANCOUVER	252	2.1	16.8	0.13	0.07	0.36
00303	VICTORIA	130	1.9	13.8	0.15	0.06	0.33

Table 12: Mean Nitrate (NO3) Loadings and Fine/Coarse Ratios
(May 1984 - December 1987)

Station Number	City	SSI(S) Dichot(D)	Number of Samples	Mean Coarse ($\mu g/m^3$)	Mean Fine ($\mu g/m^3$)	Mean Total ($\mu g/m^3$)	Mean F/C Ratio	Std. Dev. Ratio
10101	ST. JOHN'S	D	39	0.3	0.2	0.4	0.8	0.5
30101	HALIFAX	D	189	0.4	0.2	0.6	0.6	0.5
30311	SYDNEY	S	204	-	-	0.6	-	-
40201	SAINT JOHN	S	194	-	-	0.8	-	-
50104	MONTREAL	D	210	0.5	1.0	1.5	2.7	5.0
50109	MONTREAL	D	166	0.5	1.0	1.5	2.0	2.6
50307	QUEBEC CITY	D	149	0.3	0.5	0.8	2.7	16.0
60104	OTTAWA	D	206	0.4	0.5	0.9	1.3	1.9
60417	TORONTO	D	166	0.6	1.1	1.7	2.2	3.1
60204	WINDSOR	D	22	0.6	0.8	1.4	1.6	1.9
70119	WINNIPEG	D	179	0.3	0.5	0.7	2.0	3.5
80110	REGINA	S	201	-	-	0.9	-	-
90130	EDMONTON	D	185	0.3	0.7	1.0	2.6	4.9
90204	CALGARY	D	187	0.3	0.7	1.0	3.4	7.4
00118	VANCOUVER	D	181	0.5	0.6	1.1	1.5	1.9
00111	VANCOUVER	D	253	0.5	0.4	0.9	1.1	1.3
00303	VICTORIA	D	131	0.9	0.5	1.4	2.2	5.5
60104	OTTAWA	S	216	-	-	0.8	-	-
90130	EDMONTON	S	201	-	-	1.1	-	-

Table 13: Summary of Dichotomous Filter Samples Analyzed by EDXRF

Station Number	City	No. of Samples Analyzed by EDXRF	Start Date	End Date	MeanPM10 ($\mu g/m^3$) All Samples	Mean PM10 ($\mu g/m^3$) EDXRF Samples
30101	HALIFAX	50	Nov-85	Aug-87	30	26
50104	MONTREAL	54	Nov-85	Aug-87	35	32
50109	MONTREAL	40	Nov-85	Aug-87	49	48
50307	QUEBEC CITY	53	Nov-85	Jul-87	23	24
60104	OTTAWA	47	Nov-85	Aug-87	23	24
60417	TORONTO	39	Nov-85	May-87	28	27
60204	WINDSOR	67	Jul-87	Oct-88	39	37
61901	WALPOLE ISLAND	23	Jan-88	Sep-88	27	27
70119	WINNIPEG	40	Jan-86	Jul-88	31	30
90130	EDMONTON	34	Nov-85	Jul-87	37	33
90204	CALGARY	49	Nov-85	Aug-87	32	29
00118	VANCOUVER	38	Nov-85	May-87	27	30
00111	VANCOUVER	68	Nov-85	Dec-87	31	32
00303	VICTORIA	54	Nov-85	Dec-87	21	21
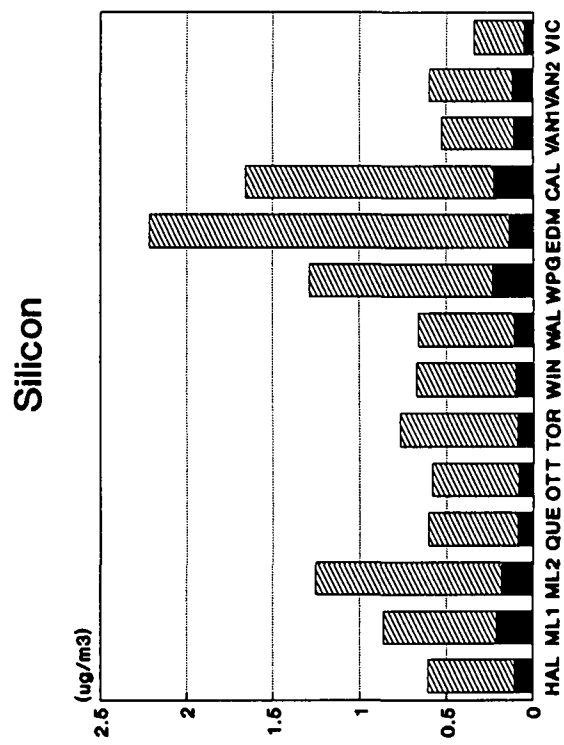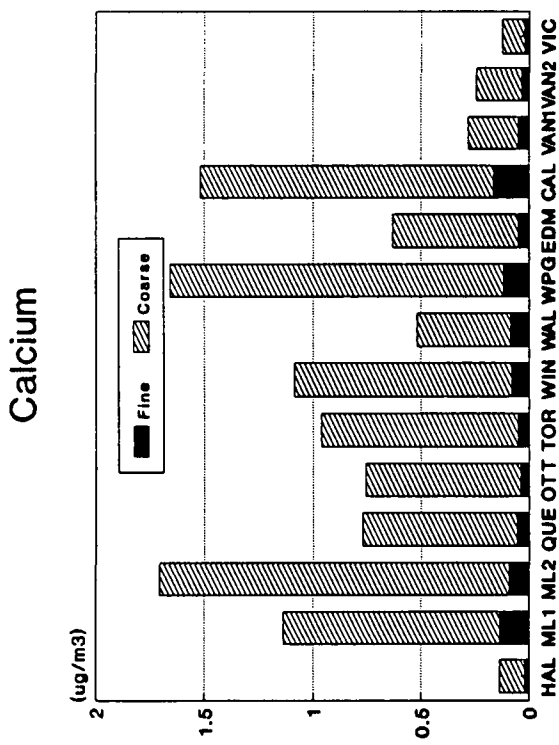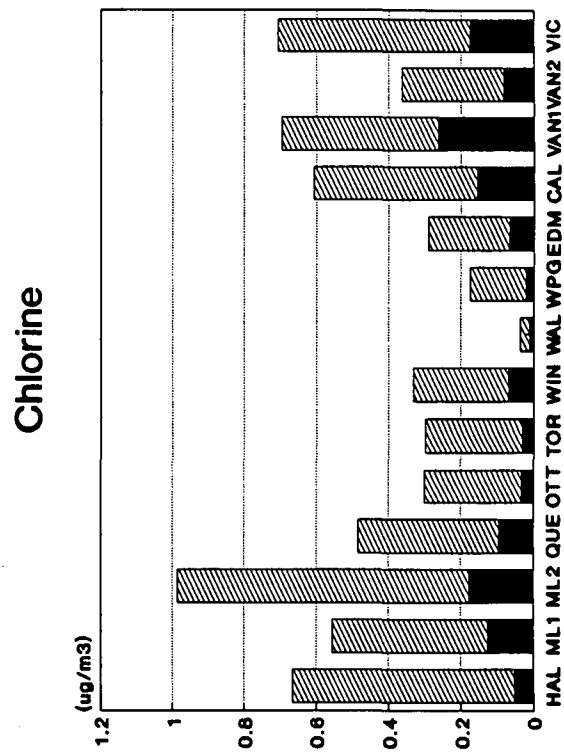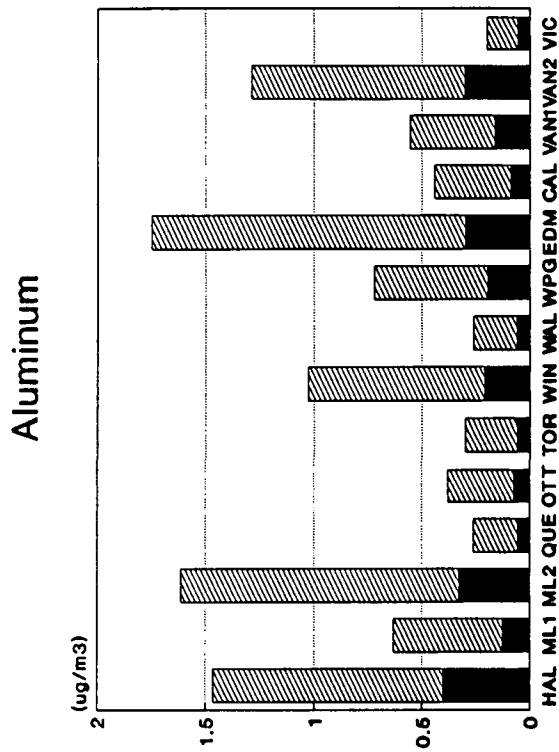
Figure 3: Mean Concentrations (µg/m³) of Selected Elements by City

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Figure 4: Mean Concentrations ($\mu g/m^3$) of Selected Elements by City

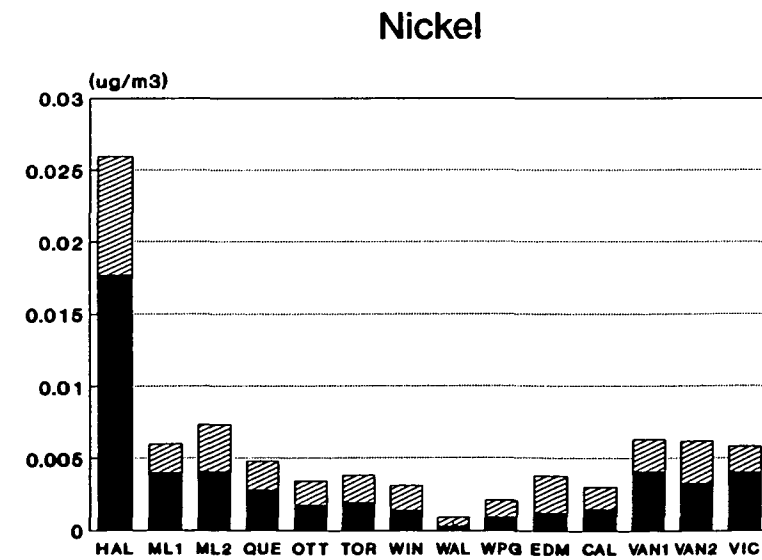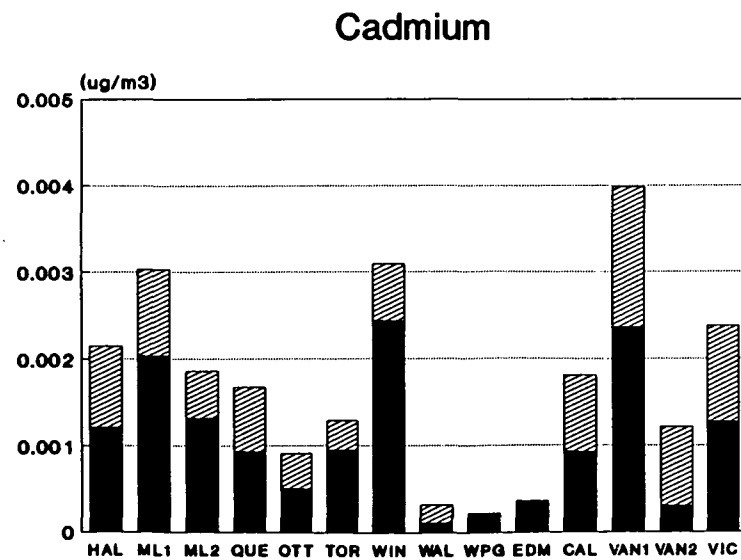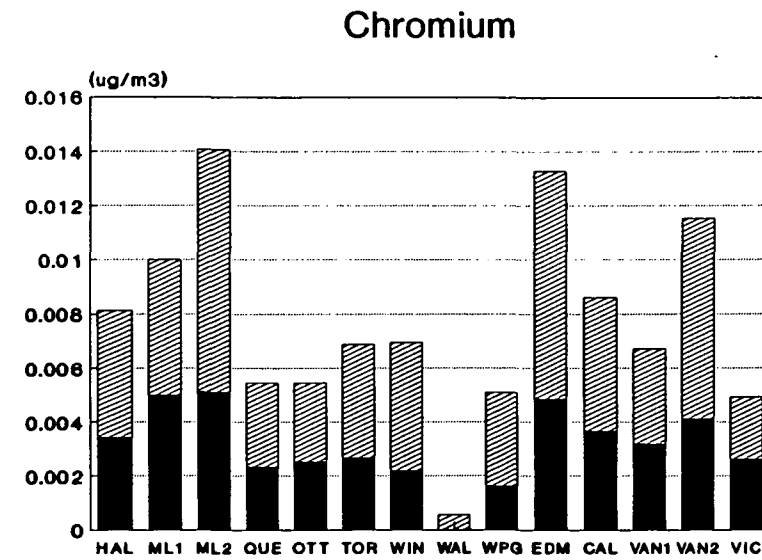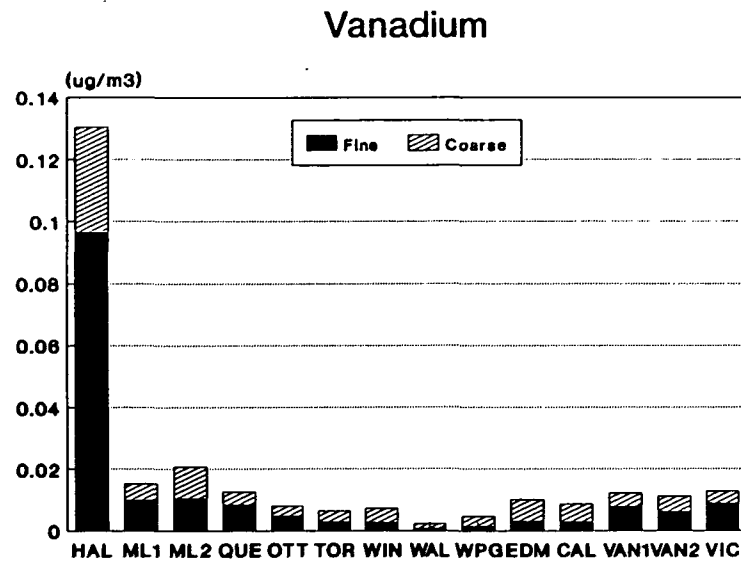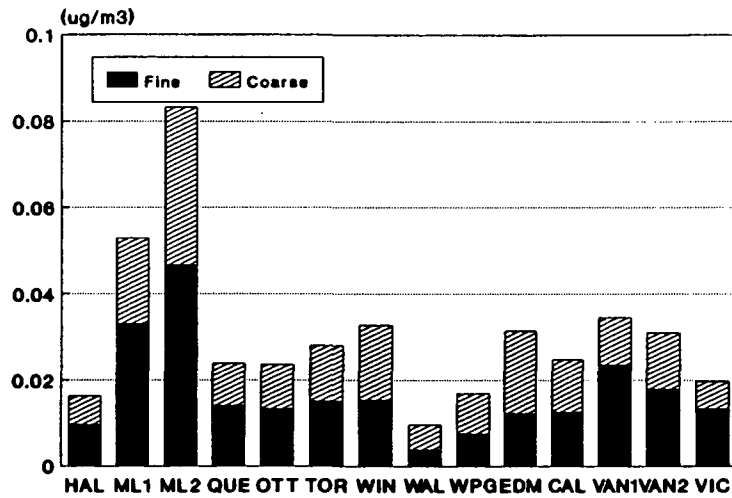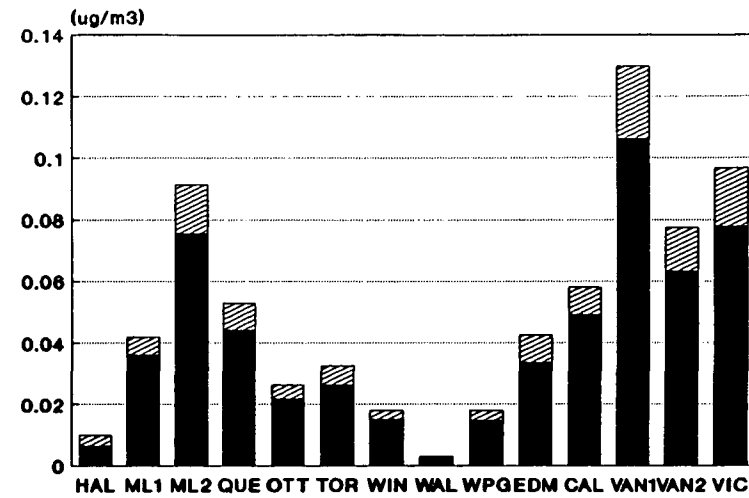Figure 5: Mean Concentrations (µg/m³) of Selected Elements by City

Manganese

Bromine

Lead
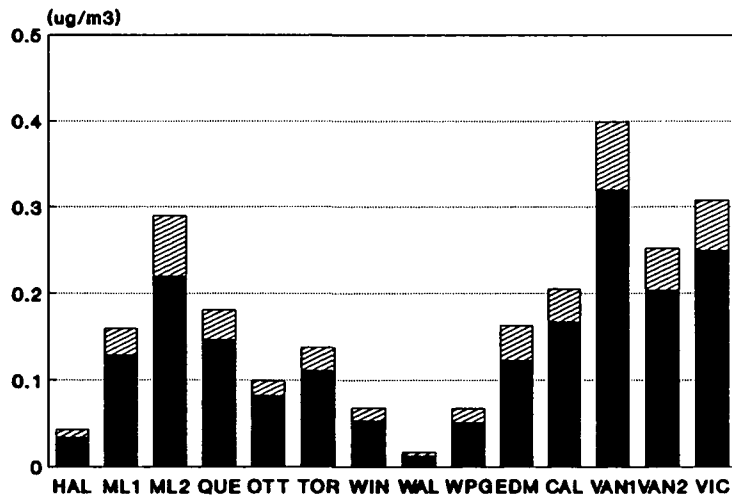

Figure 6: Mean Concentrations (μg/m³) of Selected Elements by City

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present as sulphate then the ratio of sulphates to sulphur would be 3.0. Using sulphur vs sulphate data for all dichotomous samples submitted for ion chromatography and EDXRF analysis the equation was:

$$SO_4 = 2.5\,S - 0.5 \qquad r = 0.935$$

Based on this equation, at least 15% of total sulphur is present in forms other than soluble sulphate.

A number of elements such as zinc, copper, chromium, nickel and manganese were found in significant amounts in both the fine and coarse fractions of PM_{10}. Copper concentrations are probably affected by copper emissions from the motors of co-located hi-vol samplers. At the Windsor site, hi-vol exhausts are ducted ˜10 m away from the dichotomous sampler; this site had by far the lowest copper levels of the urban sites.

Lead concentrations have decreased significantly at most monitoring sites due to a phaseout of leaded gasoline. Because leaded gasoline contains tetraethyl lead with a fixed bromine and lead content, bromine/lead ratios can be used as an indicator of automotive emission contributions to measured lead levels at monitoring sites.[14] The expected bromine/lead ratio in tailpipe emissions from automobiles using leaded gasoline is approximately 0.35. Because bromine is more volatile than lead, ambient measurements of automobile derived particulates generally show lower bromine/lead ratios. *Table 14* provides a summary of Br/Pb ratios at dichotomous sampler sites. The ratios were very consistent ranging from 0.23 to 0.30, but were lower than ratios measured in the period 1984 to 1986 which ranged from 0.3 to 0.4 at the same sites. This suggests that the automobile is still the major contributor to measured lead levels but its percentage contribution is decreasing.

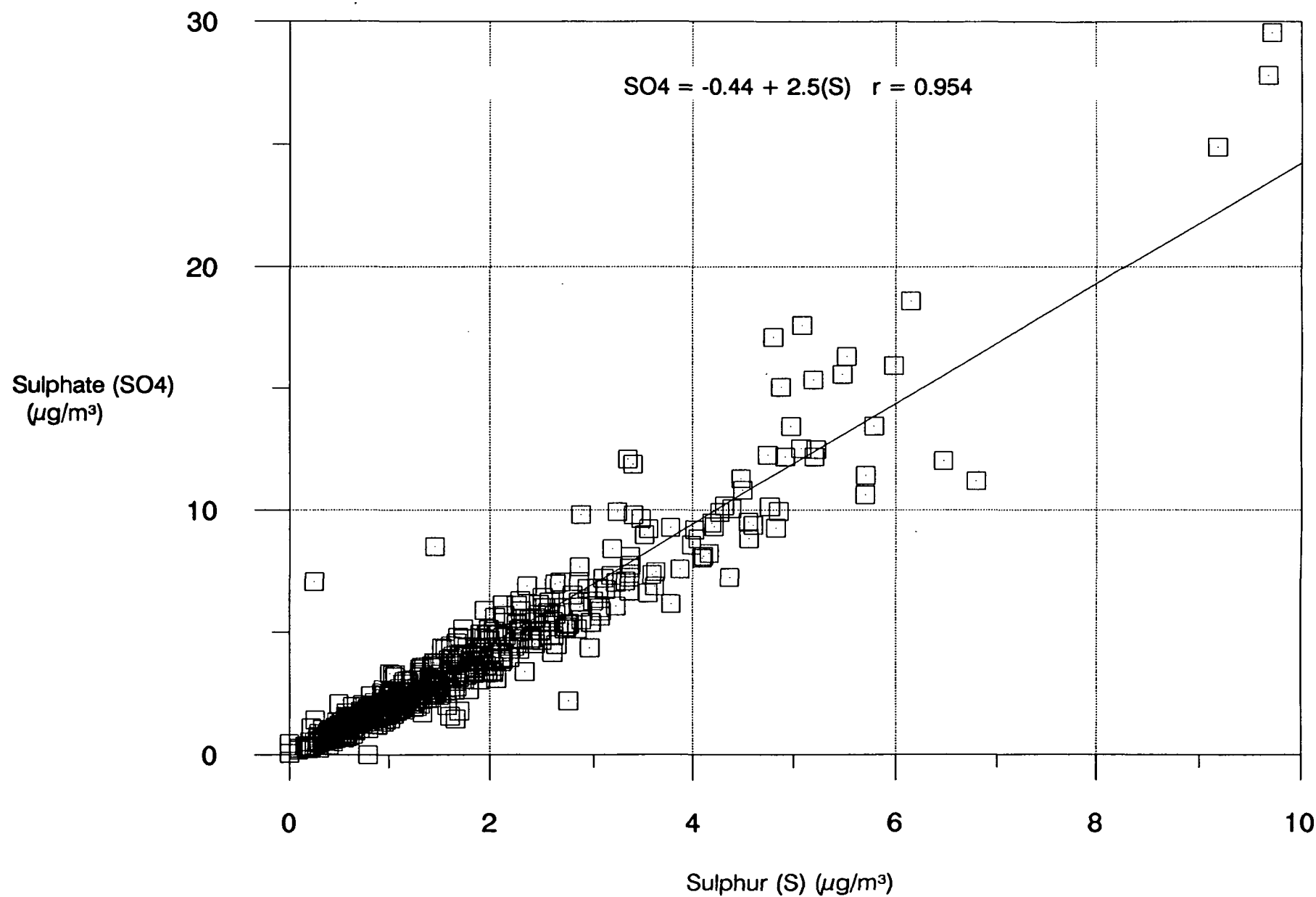## 5.3 Comparison of Dichotomous Sampler and SSI Hi-Vol

As previously noted, the SA 321 inlet used on the SSI hi-vols until January 1989 would be expected to overcollect coarse particulate matter. At two sites, Ottawa and Edmonton, co-located SSI and dichotomous samplers were operated. *Table 15* presents a comparison of mass measurements made with the two types of PM_{10} samplers, the mean ratio of the SSI hi-vol sampler mass to the dichotomous sampler mass and the slope, intercept and correlation coefficient for the linear regression of SSI PM_{10} vs dichotomous sampler PM_{10} (one outlier was removed from each data set). Scatter plots of SSI hi-vol PM_{10} vs dichotomous sampler PM_{10} are given in *Figures 8 and 9.*

The Edmonton SSI vs dichotomous sampler plot shows a large amount of scatter, a poor correlation coefficient and a large positive intercept. There are many occurrences of very high SSI mass loadings with relatively low dichotomous sampler mass loadings. The mean SSI PM_{10} concentration was 48 µg/m³ (*Table 15*) vs a mean dichotomous sampler PM_{10} concentration of 37 µg/m³.

This difference of 30% is similar to that recorded at high particulate loading sites in the United States.[6] Compared to other Canadian sites, the Edmonton site had high TSP and high coarse particulate loadings.

At the Ottawa site the SSI vs dichotomous sampler PM_{10} plot shows less scatter and a corresponding improvement in correlation coefficient. Mean PM_{10} concentrations measured by the two samplers were identical at 24 µg/m³. There were, however, a number of occurrences of large differences in PM_{10} measured by the two samplers.

Figure 7: Comparison of Sulphate and Sulphur Concentrations Dichotomous Sampler Sites (1985-1987)

$SO4 = -0.44 + 2.5(S)$ $r = 0.954$

Sulphate (SO4) (μg/m³)

Sulphur (S) (μg/m³)

Table 14: Comparison of Bromine/Lead Ratios at Dichotomous Sampler Sites
(November 1985 - October 1988)

Station	City	No. of Samples	Mean Lead (μg/m³)	Mean Bromine (μg/m³)	Mean Br/Pb Ratio	Std. Dev. Ratio	Correlation Coefficient
30101	HALIFAX	50	0.04	0.01	0.27	0.12	0.76
50104	MONTREAL	56	0.16	0.04	0.25	0.07	0.94
50109	MONTREAL	40	0.29	0.09	0.30	0.09	0.81
50307	QUEBEC CITY	53	0.18	0.05	0.28	0.06	0.98
60104	OTTAWA	47	0.10	0.03	0.24	0.05	0.99
60417	TORONTO	41	0.14	0.03	0.23	0.05	0.91
70119	WINNIPEG	40	0.07	0.02	0.27	0.04	0.96
90130	EDMONTON	34	0.16	0.04	0.25	0.03	0.97
90204	CALGARY	49	0.21	0.06	0.26	0.06	0.99
00118	VANCOUVER	38	0.40	0.13	0.30	0.04	0.99
00111	VANCOUVER	68	0.25	0.08	0.27	0.06	0.98
00303	VICTORIA	54	0.31	0.10	0.30	0.04	0.99
60204	WINDSOR	67	0.07	0.02	0.26	0.14	0.65
61901	WALPOLE ISLAND	23	0.02	0.00	0.23	0.14	0.03

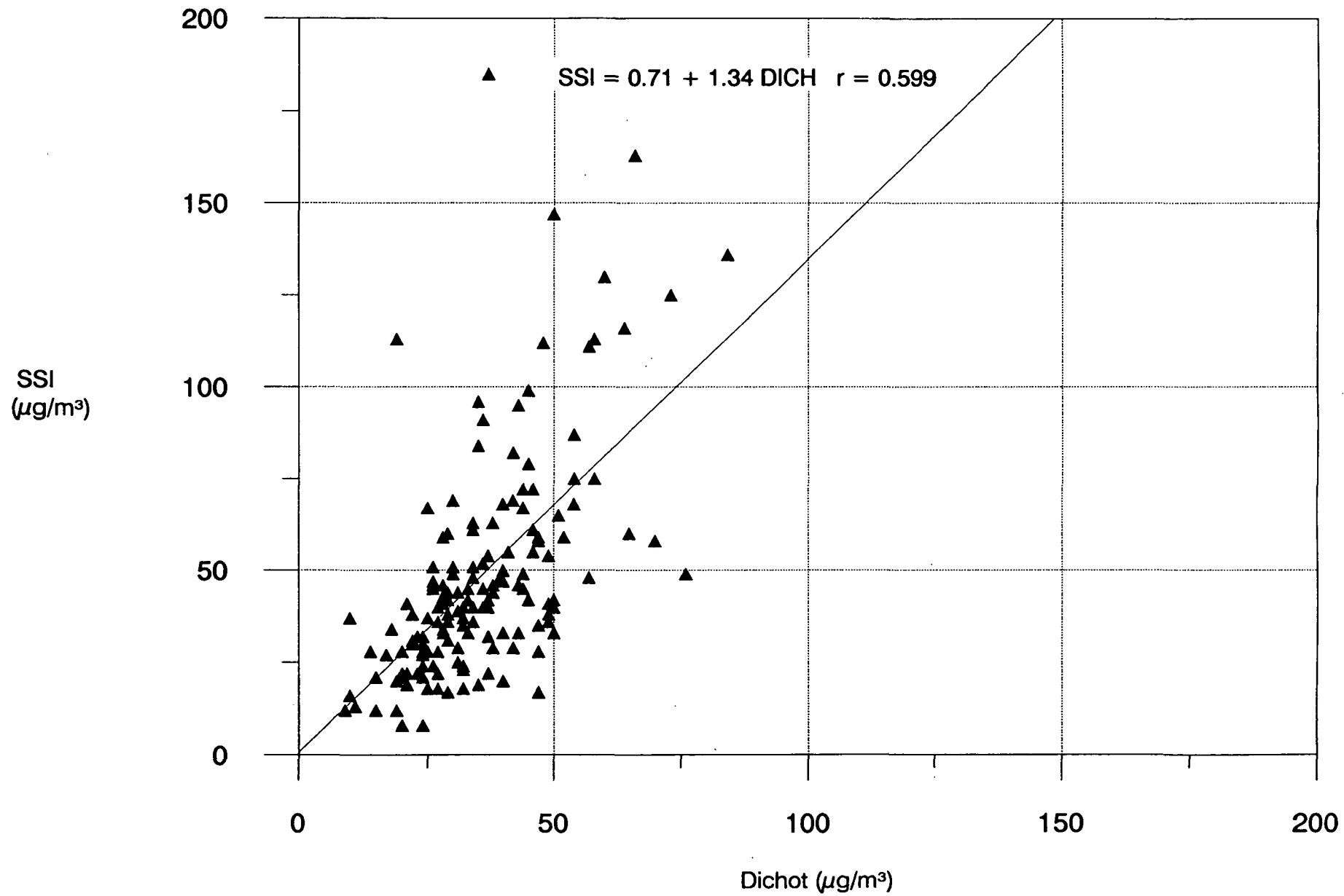Figure 8: Comparison of SSI Hi-Vol vs Dichotomous Sampler PM10
Edmonton

SSI = 0.71 + 1.34 DICH   r = 0.599

SSI (µg/m³)

Dichot (µg/m³)

Figure 9: Comparison of SSI Hi-vol PM10 vs Dichotomous Sampler PM10
Ottawa
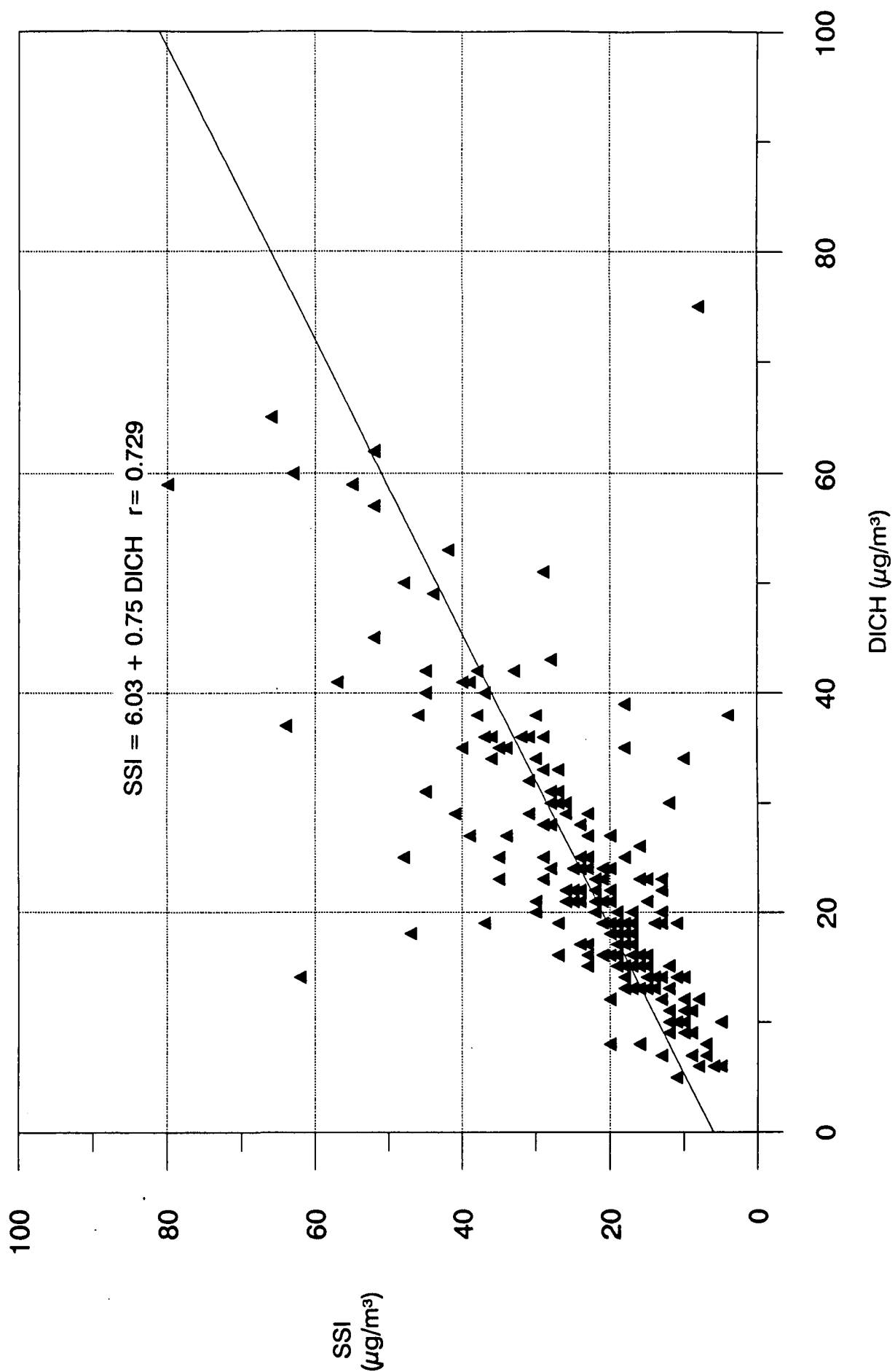
SSI = 6.03 + 0.75 DICH   r= 0.729

TABLE 15 - COMPARISON OF DICHOTOMOUS SAMPLER PM$_{10}$ AND SSI HI-VOL PM$_{10}$
(May 6, 1984 - December 29, 1987)

Station No.	City	No. of Samples	Mean Dichot PM$_{10}$ (μg/m^3)	Mean SSI PM$_{10}$ (μg/m^3)	Mean Ratio SSI/Dich	Std. Dev. Ratio	Slope	Intercept	Corr. Coeff.
60104	Ottawa	201	24	24	1.06	0.41	0.85	4.0	0.792
90130	Edmonton	156	37	48	1.35	0.75	0.84	17.3	0.459

It is difficult to estimate how large an impact the SA 321 inlet's overcollection problem had on PM$_{10}$ loadings measured at the other SSI sites (Sydney, Saint John, Regina). An examination of data collected since the changeover to the SA 1200 inlet leads will be required.

5.4 Relationships between PM$_{10}$ and TSP

The intercomparison of PM$_{10}$ and hi-vol total suspended particulates (TSP) data is important for the determination of relationships that could allow historical TSP data to be interpreted in terms of any proposed 10 μm inhalable particulate matter air quality objective.

There are many factors, however, that influence the relationships between PM$_{10}$ and TSP including (a) the variation in particle size collection efficiency of the hi-vol with varying wind speed and direction;[7] (b) artifact nitrate and sulphate formation on hi-vol filter media; (c) differences in mass measurement techniques used by the different agencies and (d) particulate losses during sample handling and sample shipment.

Table 16 contains a comparison of PM$_{10}$ and TSP mass data at each site. Shown in the table are mean concentrations of PM$_{10}$ and TSP, the mean ratio of PM$_{10}$ to TSP and the standard deviation of the ratios. Only days for which both TSP and PM$_{10}$ data were available are included in the summary.

Since hi-vols typically collect a larger size range of ambient particulate matter than do SSI or dichotomous samplers, mean PM$_{10}$/TSP ratios of less than unity would be expected. Only one site, St. John's had a ratio greater than 1.0. This site also had the lowest mean PM$_{10}$ and TSP loadings. Two sites, Halifax and Vancouver Rocky Point Park, had ratios greater than 0.80; for all other sites the mean ratios fell into the range of 0.41 to 0.78. In *Figure 10*, the ratio of PM$_{10}$ to TSP is plotted for different TSP ranges using 24 h data from all sites. The data used in the plot is contained in *Table 17*. It is clear that the ratio tends to decrease as TSP increases, the 24 h data was best fitted by a log equation as shown in the figure.

The ratio of mean PM$_{10}$ to mean TSP (1984-1987) was plotted vs mean TSP for all sites as shown in *Figure 11*. This data was also best fit by a log equation. Using the equations from *Figure 9* for 24 h data and the equation from *Figure 10* for annual data, the existing ambient air quality objectives for TSP can be translated to PM$_{10}$ as shown in *Table 18*. Since there were few data points at high concentrations, the adequacy of the derived equations is questionable for high TSP loadings (ie. equal to or greater than the tolerable). It should be noted that air quality objectives are best set based on specific health studies relating effects to specific PM$_{10}$ measurements; unfortunately, at this time little such information exists.

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Table 16: Comparison of PM10 and TSP (Mass)
(May 1984 - December 1987)

Station Number	City	SSI(S) Dichot(D)	No. of Samples	Mean PM10 (µg/m³)	Mean TSP (µg/m³)	Mean Ratio PM10/TSP	Std. Dev. Ratio
10101	ST. JOHN'S	D	35	17	18	1.25	0.85
30101	HALIFAX	D	156	30	35	0.90	0.38
30311	SYDNEY	S	166	36	60	0.63	0.30
40201	SAINT JOHN	S	183	24	39	0.67	0.29
50104	MONTREAL	D	194	35	57	0.68	0.54
50109	MONTREAL	D	138	49	111	0.49	0.24
50307	QUEBEC CITY	D	57	21	46	0.48	0.16
60104	OTTAWA	D	208	23	40	0.59	0.21
60417	TORONTO	D	159	28	55	0.53	0.21
60204	WINDSOR	D	20	37	69	0.53	0.18
70119	WINNIPEG	D	163	31	70	0.54	0.30
80110	REGINA	S	190	37	57	0.78	0.49
90130	EDMONTON	D	165	36	90	0.48	0.25
90204	CALGARY	D	185	32	86	0.41	0.21
00118	VANCOUVER	D	108	27	38	0.71	0.19
00111	VANCOUVER	D	155	31	40	0.81	0.28
00303	VICTORIA	D	113	21	39	0.55	0.27
60104	OTTAWA	S	207	24	40	0.60	0.22
90130	EDMONTON	S	195	46	80	0.63	0.32

Figure 10:PM10/TSP Ratio vs TSP Concentrations
(All 24 h Data 1984-1987)

$$PM10/TSP = 1.50 - 0.49 * \log(TSP) \quad r = 0.928$$

PM10/TSP Ratio
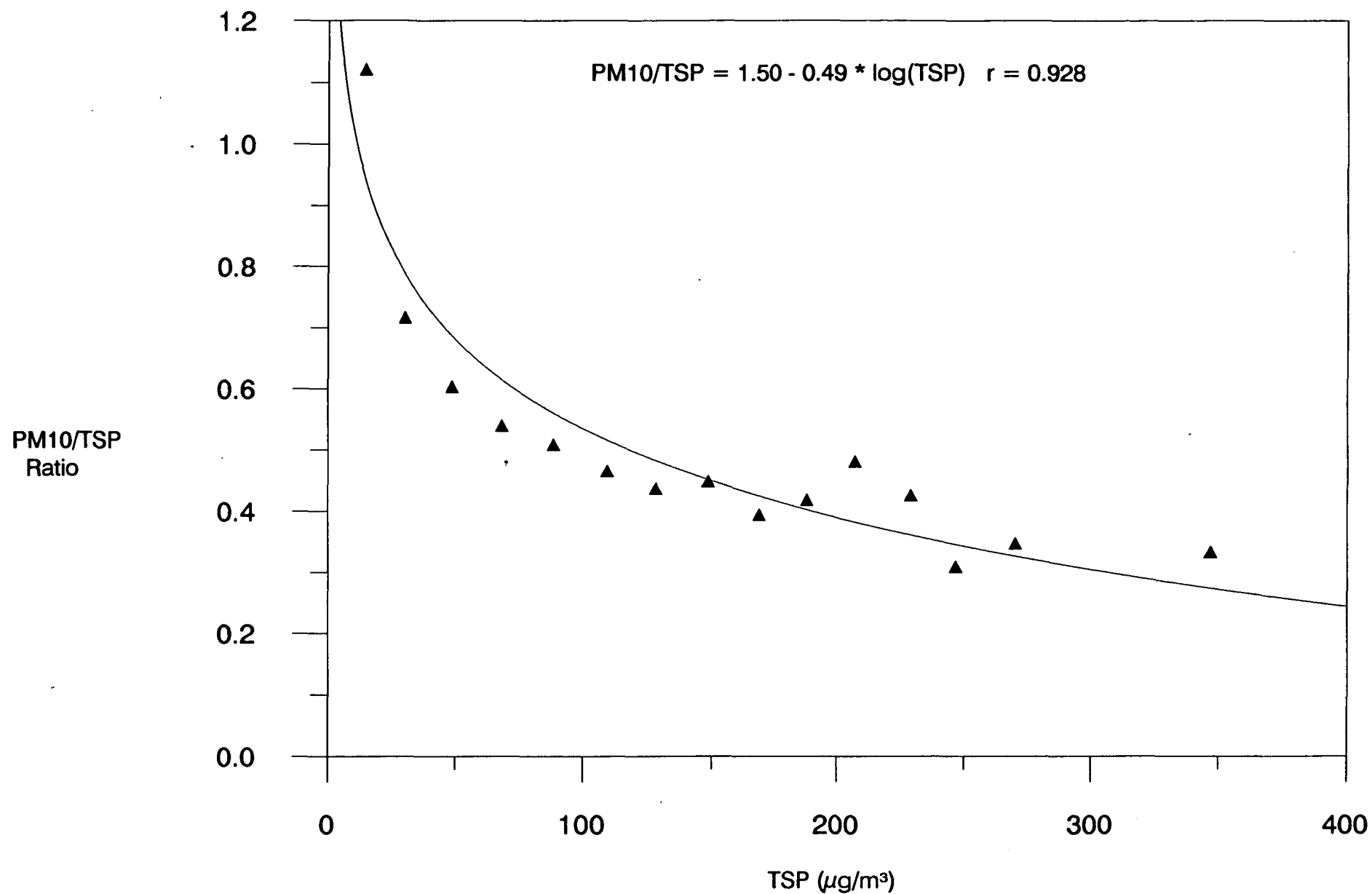
TSP ($\mu g/m^3$)

Table 17: Mean PM10/TSP Ratio by TSP Range

TSP Range (μg/m³)	No. of Samples	Mean TSP (μg/m³)	Mean PM10 (μg/m³)	Mean PM10/TSP Ratio
0 - 19	173	14.5	14.9	1.12
20 - 39	794	30.1	21.3	0.72
40 - 59	659	48.7	29.4	0.60
60 - 79	361	68.6	37.0	0.54
80 - 99	181	88.7	44.9	0.51
100 - 119	113	109.5	51.0	0.47
120 - 139	69	128.6	56.0	0.44
140 - 159	24	148.7	66.7	0.45
160 - 179	33	169.0	66.7	0.39
180 - 199	14	188.2	78.9	0.42
200 - 219	10	207.1	99.5	0.48
220 - 239	10	229.1	97.4	0.43
240 - 259	5	246.8	76.4	0.31
260 - 279	3	270.0	93.3	0.35
280 - 439	6	347.0	109.7	0.33